AD-A051 088   NEW YORK UNIV N Y DEPT OF CHEMISTRY   F/G 7/4
                 STUDY OF ADSORPTION AT THE LIQUID-SOLID INTERFACE BY SPECTROSCO--ETC(U)
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FINAL REPORT

PROJECT NR 056-515

Contract No. N00014-67-A-0467-0023

EAM TITLE: LIQUID-SOLID INTERFACE

STUDY OF ADSORPTION AT THE LIQUID-SOLID INTERFACE

BY SPECTROSCOPIC TECHNIQUES

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October 1, 1974

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Study of Adsorption at the Liquid-Solid Interface by Spectroscopic Techniques.		5. TYPE OF REPORT & PERIOD COVERED Final Report 1 May 71 - 31 Dec 73 5/1/71 - 12/31/73
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. J. D. Low		8. CONTRACT OR GRANT NUMBER(s) N00014-67-A-0467-0023
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry New York University New York, N.Y. 10003		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project No. NR 056-515
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Virginia 22170		12. REPORT DATE 10/1/74 1 Oct 74
		13. NUMBER OF PAGES 5 44 P.
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Infrared Spectra
Fourier transform spectroscopy
Adsorption from solution
Water, infrared spectra

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This is the final report of a project concerned with the general topic of adsorption at the liquid-solid interface. Publications resulting from the work are:

[see over]

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1 JAN 73
S/N 0102-014-6601
406 817

JOB   Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

1) The Fundamental Infrared Spectrum of the Ammonium Ion in Aqueous Solution. M.J.D. Low and R.T. Yang, Spectroscopy Letters 5(8), 245 (1972).

2) Infrared Study of Adsorption in situ at the Liquid/Solid Interface. IV. The Utility of Internal Reflection Techniques. R.T. Yang and M.J.D. Low, G.L. Iäller and J. Fenn, Journal of Colloid and Interface Science 44, 249 (1973).

3) Infrared Study of Adsorption in situ at the Liquid/Solid Interface. V. Adsorption of Octadecanol, Octadecylamine, and Octadecanedioic Acid on Silica, and a Criterion of Considering Competitive Adsorption. M.J.D. Low and P.L. Lee, Journal of Colloid and Interface Science 45, 148 (1973).

4) Infrared Spectra of Water in Aqueous Solutions Using Internal Reflection Spectroscopy. M.J.D. Low and R.T. Yang, Spectroscopy Letters 6(5), 299 (1973).

5) Quantitative Analysis of Aqueous Nitrite/Nitrate Solution by Infrared Internal Reflectance Spectrometry. R.T. Yang and M.J.D. Low, Analytical Chemistry 45, 2014, 1973.

6) Infrared Internal Reflection Spectra of Methanol-Water Mixtures. R.T. Yang and M.J.D. Low, Spectrochimica Acta 30A, 1787 (1974).

Conclusions

1) Infrared Transmission spectroscopy is an extremely useful tool for obtaining detailed mechanistic information about adsorbate-adsorbent interactions at the solid-liquid interface.

2) Internal reflection techniques can also be used to study "adsorption from solution," but studies involving adsorption directly onto internal reflection optics are of limited utility.

3) Further work is needed to permit the use of internal reflection techniques for studies of adsorption onto powders, and to permit the use of laser Raman spectroscopy for the study of adsorption from solution.

4) Fourier transform spectroscopy can yield extremely good infrared spectra of water and aqueous solutions. The techniques offer a potentially very useful approach to the study of the structure of water and aqueous solutions and solvent-solute interactions.

Final Report of Project NR 056-515

Period

This report covers the activities of the project for the period from May 1, 1971 through December 31, 1973.

Professional Personnel

M. J. D. Low, Ph.D., Principal Investigator
R. T. Yang, Ph.D., Assistant Research Scientist
H. Mark, Ph.D., Assistant Research Scientist
A. Ravi, Ph.D., Assistant Research Scientist
P. L. Lee, Ph.D., Assistant Research Scientist

(all part-time)

Topic

This project is concerned with the general topic of the study of adsorption at the liquid-solid interface by spectroscopic techniques.

Reports

Two Annual Reports dated July 1, 1972 and October 1, 1973 were distributed. Five Technical Reports dated September 1, 1972, October 1, 1972, November 1, 1972, January 30, 1973, and October 1, 1974, were distributed.

Publications

Six publications resulted from the work of the project:

(1) The Fundamental Infrared Spectrum of the Ammonium Ion in Aqueous Solution. M. J. D. Low and R. T. Yang, Spectroscopy Letters 5(8), 245 (1972).

(2) Infrared Study of Adsorption in situ at the Liquid/Solid Interface. IV. The Utility of Internal Reflection Techniques. R. T. Yang and M. J. D. Low, G. L. Haller and J. Fenn, Journal of Colloid and Interface Science 44, 249 (1973).

(3) Infrared Study of Adsorption in situ at the Liquid/Solid Interface. V. Adsorption of Octadecanol, Octadecylamine, and Octadecanedioic Acid on Silica, and a Criterion of Considering Competitive Adsorption. M. J. D. Low and P. L. Lee, Journal of Colloid and Interface Science 45, 148 (1973).

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(6) Infrared Internal Reflection Spectra of Methanol-Water Mixtures. R. T.
Yang and M. J. D. Low, Spectrochimica Acta 30A, 1787 (1974)

Summary

Technical details of the work performed during the course of this pro-
ject are given in the five technical reports issued individually and in the
six publications appended to this report.

The general work topic of this project was "adsorption from solution,"
i.e., a study of adsorbate-adsorbent interaction at the solid-liquid inter-
face, using spectroscopic methods. Four related topics are involved.

1. Infrared Transmission Spectroscopy

Earlier work employing infrared transmission spectroscopy of molecular
species adsorbed at the liquid-solid interface was extended, and is described
in the appended reprint 3. In addition to obtaining detailed information
about the interaction of some long-chain molecules with surface silanols, it
was possible to suggest a criterion for considering competitive adsorption
from solution.

2. Infrared Internal Reflection Spectroscopy

The utility of internal reflection techniques was explored. A portion
of the study, involving the adsorption of molecules directly onto internal
reflection elements, was quite successful and is described in detail in the
appended reprint 2. Another part was not successful.

Attempts were made to use internal reflection techniques to study ad-
sorption onto powders. What is involved is this: a powdered adsorbent is
placed onto the surface of the internal reflection prism. The composite is
then exposed to solution, and adsorption occurs onto the surface of the
powdered adsorbent. The intent of the measurement is to record the spectrum
of the layer of the adsorbed material on the surface of the powder. Attempts
were made to obtain spectra of carboxylic acids adsorbed onto ZnO, SiO_2, Al_2O_3,
and TiO_2, but the measurements were not successful. Greater instrumental
sensitivity was needed.

3. Laser Raman Spectroscopy

Attempts were made to use laser Raman spectroscopy to study adsorption
from aqueous solution. The general aspects of the measurements are as follows.
An adsorbent is submerged in water in which a small amount of material such
as stearic acid is dissolved. The stearic acid, i.e., the adsorbate becomes
bound to the surface of the adsorbent, and a spectrum is recorded. The spectrum
would show the absorptions of the solid adsorbent itself and also of the
surface layer. The measurement is carried out while the adsorbent is still

submerged in the solution, so that the measurements are carried out "in situ," so that there is no chance of disturbing the surface layer by removing the adsorbent from the solution. The presence of the solute in solution would not be detected because the solutions are very weak. Experiments of the type outlined were carried out both with aqueous and nonaqueous solutions, in attempts to learn how to carry the measurements out. Measurements were made with the adsorbent submerged, and also with adsorbent which had been submerged and then removed from solution. The only positive results which were obtained were with a sample of ZnO which had been immersed in a solution of stearic acid in CCl_4 so that stearic acid became adsorbed on the surface of the sample, and which was then removed from the solution. Raman spectra of the sample, carried out with the sample in air, showed the bands of adsorbed stearic acid. When the sample was placed in the solution again, and a Raman spectrum of the submerged sample was recorded, the spectrum was very poor. Similar experiments with aqueous solutions led to this conclusion: while it was possible to detect evidence of adsorbed material when the sample was examined in air, it was not possible to detect chemisorbed surface species when the sample was submerged because the intensity of the scattered rays was too weak. Rough tests showed that when a powdered adsorbent was submerged in water, the scattering decreased by an order of magnitude, so that the resulting spectrum was so weak that the bands of adsorbed species could not be detected. The problem was thus an insolvable one with the equipment at hand. It will probably be possible to use Raman spectroscopy, however, if the techniques are made more sensitive.
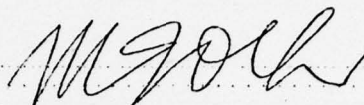
4. Infrared Spectra of Water and Aqueous Solutions.

Work in this area was needed to define to what extent the use of water would interfere with infrared measurements. It was found that, using the techniques described in the reprints 1,2,4,5, and 6, infrared spectra of pure water, of water solvent, and of solutes, could be recorded extremely well. In particular, the use of infrared Fourier transform spectroscopic techniques in conjunction with internal reflection devices makes it possible to obtain infrared spectroscopic data on water and aqueous solutions much better than those obtainable with dispersion spectrometers.

Conclusions

1) Infrared Transmission spectroscopy is an extremely useful tool for obtaining detailed mechanistic information about adsorbate-adsorbent interactions at the solid-liquid interface.

2) Internal reflection techniques can also be used to study "adsorption from solution," but studies involving adsorption directly onto internal reflection optics are of limited utility.

3) Further work is needed to permit the use of internal reflection techniques for studies of adsorption onto powders, and to permit the use of laser Raman spectroscopy for the study of adsorption from solution.

4) Fourier transform spectroscopy can yield extremely good infrared spectra of water and aqueos solutions. The techniques offer a potentially very useful approach to the study of the structure of water and aqueous solutions and

solvent-solute interactions.

M. J. D. Low
Principal Investigator

THE FUNDAMENTAL INFRARED SPECTRUM OF THE AMMONIUM ION IN AQUEOUS SOLUTIONS

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The infrared absorptions of NH_4^+ of aqueous solutions of NH_4^+ salt solutions were recently considered in some detail and, based on changes in the contour of the water band, the effect of anions of the water absorption were discussed.[1] We find, however, that differences of the contours of absorptions of pure water and of aqueous solutions can easily produce an artifact.

We have measured infrared spectra of water and of aqueous solutions using a modified[2] Digilab Inc. Model FTS-14 Fourier transform spectrometer and, to avoid the difficulties brought about by the use of very thin transmission cells, have employed ATR techniques using a Ge prism in a suitable attachment.[3] The equilvant total penetration depth was estimated to be 1.9μ at 3400 cm^{-1}, the molar extinction coefficient of water[4] being taken as 81 at 3400 cm^{-1}. Spectral data were obtained over the $3800-800$ cm^{-1} region, using 400 scans at a resolution of 8 cm^{-1} constant over the entire region for each spectrum. Only single-beam data were measured, always using the same ATR prism under identical conditions. However, single-beam spectra were stored, retrieved, and ratioed by computation as required, using the instrument's digital computer. The ratioing process is equivalent to using a dispersion spectrometer in

the double-beam mode with cells of precisely the same path-
lengths in each beam, thus "compensating" one liquid with
another. This equivalency is precise only when the two liq-
uids whose spectra are ratioed have identical refractive in-
dices, so that the equivalent penetration depths for the two
liquids are the same. In the present case, however, the in-
dex matching[5] was good, so that the equivalent pentration
depths for all liquids were very close; that this was so was
shown by the identical absorptions obtained at 3400 cm^{-1}.

Examples of single-beam and ratioed spectra are shown
in Fig. 1. Expanded segments of some spectra of 2M NH_4NO_3
solutions are shown in Fig. 2.   Two bands near 3050 and
2880 cm^{-1} appeared in ratioed spectra obtained by using the
spectrum of water as "reference." However, a new band near
3200 cm^{-1} appeared in spectra employing a saturated NaCl so-
lution as reference in the manner employed earlier.[1] The
3050 and 2880 cm^{-1} bands were superimposed on the prominent
3200 cm^{-1} band. The ratioed trace B of Fig. 2 was thus equiv-
alent to the spectra of NH_4NO_3 solution "compensated" with
saturated NaCl solution reported earlier, i.e. spectra re-
corded with NH_4NO_3 solution in one beam and NaCl solution in
the reference beam.[1] Similarly, trace C of Fig. 2 is the
spectrum of H_2O "compensated" with saturated NaCl solution;
a 3200 cm^{-1} band was again produced.

Fig. 3 shows scale-expanded segments of spectra of NH_4Cl
and $NH_4H_2PO_4$ solutions, "compensated" with water, saturated
NaCl, or $NaClO_4$ solutions. Such ratioed spectra are equiv-
alent to others presented earlier[1], and show the two 3050
and 2880 cm^{-1} bands as well as a band near 3200 cm^{-1}. How-
ever, the spectrum of $NaClO_4$ solution was also ratioed a-
gainst that of saturated NaCl solution (D, Fig. 2), and the
3200 cm^{-1} band was again produced. In all cases, the max-
imum of the 3200 cm^{-1} band shifted slightly toward lower fre-

quencies when the concentration of solutions was increased, as observed earlier.[1]

The effects of solutes on the structure of water are well-known, and it appears that the 3200 cm^{-1} band was an
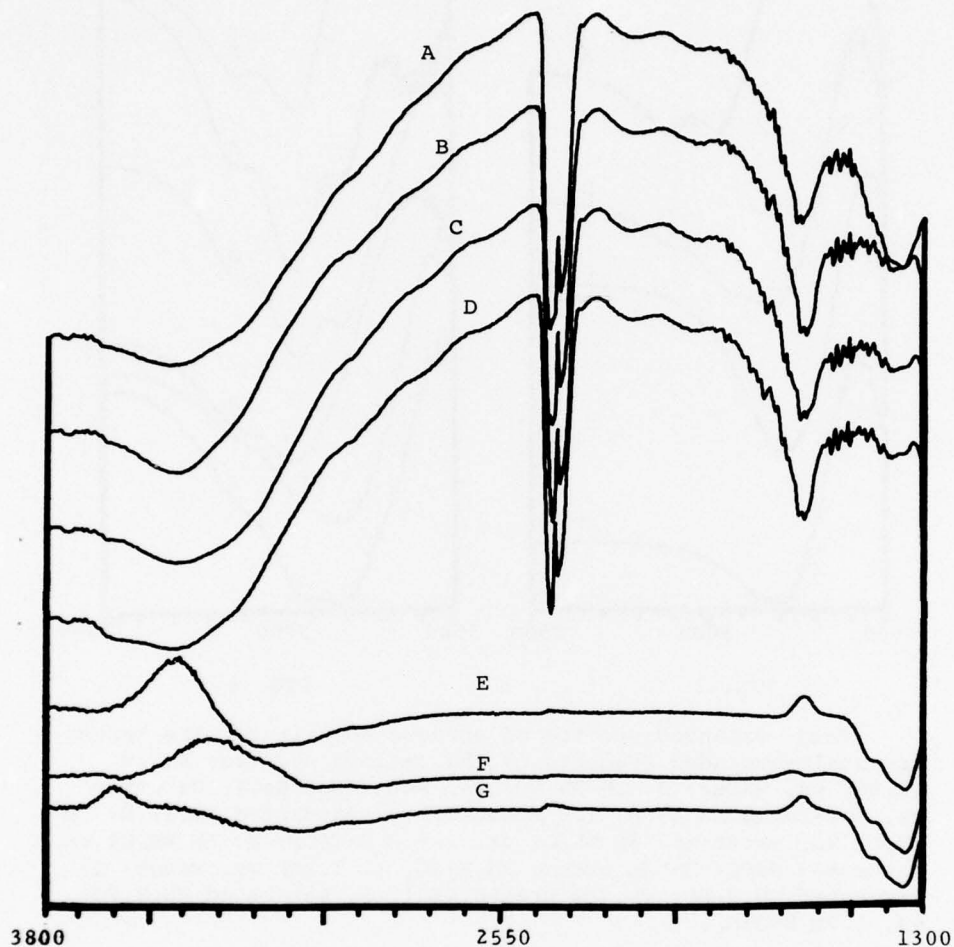
FIG. I

Spectra of aqueous solutions; spectra A-D are single-beam spectrum of A: 2M NH_4NO_3; B: saturated NaCl; C: water; D: 1.9 M $NaClO_4$. Spectra E-G are ratioed spectra of: E: 2M NH_4NO_3 vs. saturated NaCl; F: 2M NH_4NO_3 vs. water; G: 2M NH_4NO_3 vs. 1.9 M $NaClO_4$. Scale-expanded segments are shown in Fig. 2.

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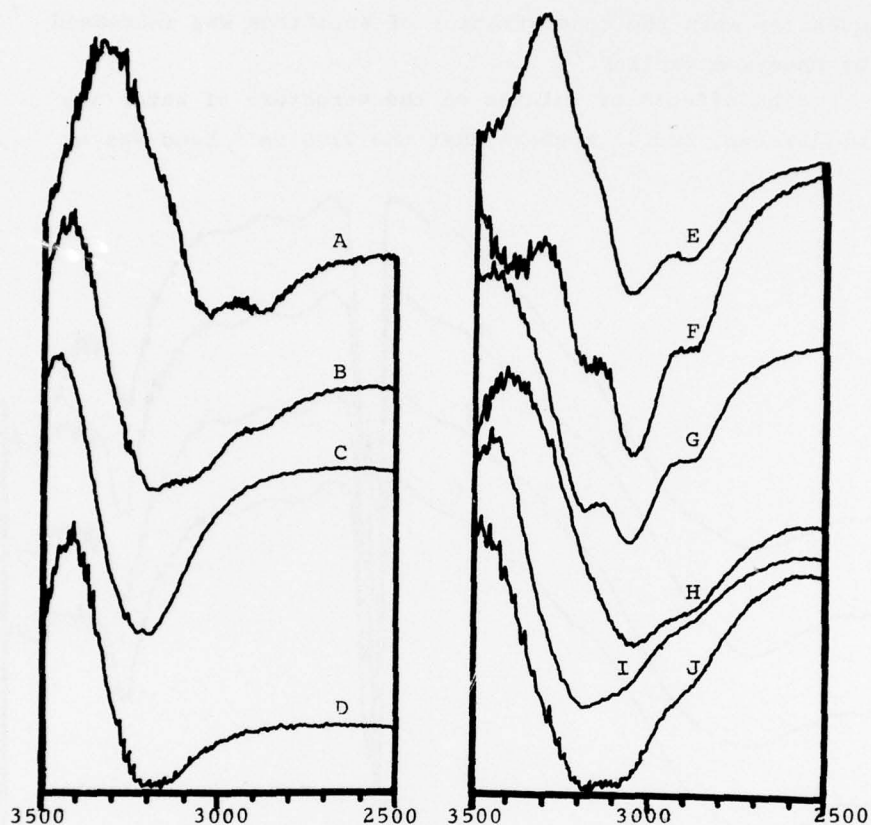
FIG. 2   FIG. 3

Scale-expanded spectra of aqueous solutions. The traces are scale-expanded segments of the ratioed spectra; A: 2M NH_4NO_3 vs. water; B: 2M NH_4NO_3 vs. saturated NaCl; C: water vs. saturated NaCl; D: 1.9 M $NaClO_4$ vs. saturated NaCl; E: 5M NH_4Cl vs. water; F: 5M NH_4Cl vs. 1.9 M $NaClO_4$; G: 5M NH_4Cl vs. saturated NaCl; H: saturated $NH_4H_2PO_4$ ($\sim$ 1.6M) vs. water; I: saturated $NH_4H_2PO_4$ vs. saturated NaCl; J: saturated $NH_4H_2PO_4$ vs. 1.9M $NaClO_4$.

artifact brought about by the differences of structure-breaking effects of Na^+, Cl^-, ClO_4^- and other ions[6] leading to changes in the contours of the water bands of the solutions. Consequently, the earlier assignment[1] of the 3200 cm^{-1} band

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to the NH_4^+ ν_3 mode, and other assignments, are suspect. It
seems better to attribute the 3050 cm^{-1} band to the asym-
metric stretching mode and the 2875 cm^{-1} band to a combina-
tion of fundamentals. This new assignment is consistent with
the observation of the high deformation frequency of NH_4^+ [1,7].
Also, the water band contours can be expected to differ de-
pending on the nature and concentration of the solute, and
such effects seem but little explored. Interpretations of
the spectra of aqueous solutions in terms of the structure
of the solvent-and probably of all highly associated liquids-
must thus be approached with caution.

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Infrared Study of Adsorption *in situ* at the Liquid/Solid Interface
IV. The Utility of Internal Reflection Techniques [1]

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Experiments were carried out to explore the feasibility of using internal reflection spectroscopy to study adsorption phenomena *in situ* at the liquid/solid interface. To test the methods, stearic acid was adsorbed from CCl_4 solution directly onto the surfaces of Ge and Al_2O_3 internal reflection prisms which acted as adsorbents. Infrared spectra of the adsorbed layer were measured with a Beckman IR-12 and also a Digilab FTS-14 Fourier transform spectrometer. It was possible to follow the build-up of the adsorbed layer as function of time and, with solutions of various concentrations, to note changes in the total adsorption as function of concentration. The maximum amount adsorbed was about 0.3 monolayer with solutions in the 10^{-4}–10^{-2} M range. The lowest coverage observed was about 0.03 monolayer. Some information about the orientation of the adsorbed species could be obtained through the use of polarized radiation. Although the method is restricted to adsorbates which can be fashioned into internal reflection elements, the techniques are suitable for obtaining information about kinetics of adsorption and desorption, adsorption isotherms, adsorbate–adsorbent perturbations, the orientation and structure of the absorbed layer, and chemisorption.

INTRODUCTION

The topic of "adsorption from solution" has received widespread attention for many years because of its technological and scientific importance. However, despite a voluminous literature, there is little in the way of definite information concerning the nature and structure of adsorbed species formed on the surfaces of solids submerged in liquids, although much has been inferred on the basis of indirect measurements (1–3) such as adsorption isotherms or electrochemical effects.

Some direct information about surface species has been obtained by means of infrared spectroscopy using transmission/ab-

[1] Part III: Ref. (8).
[2] To whom inquiries should be addressed.

sorption techniques (4–8). The latter are useful, but, when carried out *in situ* under controlled conditions (6–8), present some formidable experimental difficulties. Obtaining infrared spectra of surface species by means of the techniques of internal reflection spectroscopy, reviewed by Harrick (9), seemed an alternate and attractive approach. We have consequently explored the feasibility of using infrared internal reflection techniques for studying adsorption *in situ* at the liquid/solid interface, using internally reflecting prisms as substrates.

In contrast to transmission/absorption techniques, where the solid is finely divided to provide a large surface area bearing numerous surface species which can be "sampled" by the infrared beam, the internal reflection tech-

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niques dictate the use of solids of quite small surface area; although multiple reflections are used, the sample *per se* is small, and relatively great demands are placed on the instrumentation needed to record spectra. Consequently, a secondary objective was to explore the utility of carrying out the internal reflection measurements with a Fourier transform spectrometer, as well as with a dispersion spectrometer. With these limited objectives in mind, we have chosen stearic acid as adsorbate because our previous experience with adsorbed acids was useful, CCl_4 as solvent mainly because of its spectroscopic properties, and Ge as IRE because its high index of refraction would lead to proper index matching and would allow 45° reflections, the choices being made to minimize instrumental problems because it was intended to explore the feasibility and demonstrate the utility of the technique.

EXPERIMENTAL METHOD

Some infrared spectra were recorded with a Beckman IR-12 spectrophotometer operating conventionally in the double-beam mode, using ordinate and abscissa scale expansions are required, in conjunction with a Model 9 internal reflection accessory and MIR-6 sample holder supplied by Wilks Scientific Corporation. Polarization measurements employed a
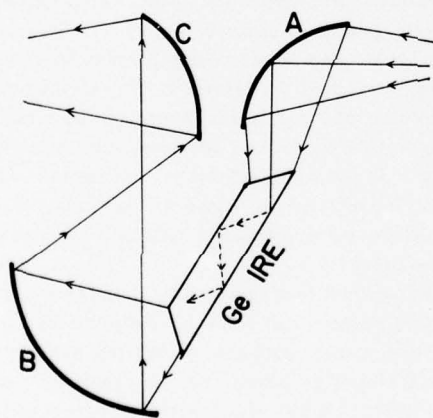
FIG. 1. Internal reflection accessory used with the FTS-14 Fourier transform spectrometer.

Perkin-Elmer wire grid polarizer. Other infrared spectra were recorded with a Digilab, Inc. Model FTS-14 Fourier transform spectrometer modified for single-beam operation as described elsewhere (10). The FTS-14's relatively large infrared beam required the construction of the device shown in Fig. 1. Mirror A of Fig. 1 was a 90° torroid used deliberately in an optically improper fashion: by rotating A by 90° through one axis, the image of the circular incident beam was not circular, but was distorted into a rectangle roughly matching the rectangular cross section of the end of the internal reflection element (IRE). Mirror B was a gold-coated, first-surface, concave Pyrex prism. Mirror C was a 60° torrid which reshaped the beam and passed it on to the FTS-14's detector. The device transmitted approximately 20% of the total incident beam. The Ge IREs were supplied by Harrick Scientific Corporation and were held by a Wilks MIR-6 sample holder.

All the spectra shown are "noisy." The too frequently employed practice of displaying traces from which all noise has been removed by a simple manual deletion has been avoided.

Spectroscopic-grade CCl_4, 99% pure stearic acid from Nutritional Biochemicals Corporation, and other reagent-grade materials were used without further purification. The IREs, described where appropriate, were cleaned prior to use with hot (50–70°) chromic acid cleaning solution, HNO_3, and distilled water. The HNO_3 treatment was done to displace residual chromium ions. As long as the cleaning period and temperature are carefully controlled, the cleaning procedure results in a thin surface oxide layer on the Ge. The oxide layer remains thin with respect to the penetration depth, and electric fields at the interface are still defined by the Ge/CCl_4 indices of refraction. All experiments were carried out at room temperature, nominally 25°.

In order to carry out quantitative measurements, a calibration is needed and can be provided by measuring the absorbance of a stearic acid monolayer deposited on the IRE

surface (11). The absorbance of the methylene asymmetric stretching band at 2928 cm^{-1} (A_{2928}) serves as a measure of the amount of stearic acid present on the IRE. The methylene groups near the carboxyl group of an adsorbed stearic acid molecule would be more perturbed than methylene groups elsewhere on the hydrocarbon chain, so that absorbance per methylene group would vary somewhat depending on its position along the chain (12), but for purposes of calibration the methylene absorbance was assumed to be constant. The absorbance of methylene groups of adsorbed stearic acid is ratioed against the absorbance of a deposited stearic acid monolayer, so that the amount of adsorbed stearic acid can be determined. Alternatively, the methylene absorbance of 0.4 of a compressed monolayer of calcium stearate deposited on a sapphire surface was used (4); the sapphire plate gave 100 reflections at 45°. A conversion from the sapphire system to the germanium system is

$$\frac{A_{\text{sapph/st/air}}}{A_{\text{Ge/st/CCl}_4}} = \frac{\dfrac{n_{\text{st}}}{n_{\text{sapph}}}\left[1 - \left(\dfrac{n_{\text{CCl}_4}}{n_{\text{Ge}}}\right)^2\right]\alpha}{\dfrac{n_{\text{st}}}{n_{\text{Ge}}}\left[1 - \left(\dfrac{n_{\text{air}}}{n_{\text{sapph}}}\right)^2\right]\beta} = 1.92$$

$$\alpha = 1 + \frac{\left[1 + \left(\dfrac{n_{\text{air}}}{n_{\text{st}}}\right)^4\right]\sin^2\theta - \left(\dfrac{n_{\text{air}}}{n_{\text{sapph}}}\right)^2}{\left[1 + \left(\dfrac{n_{\text{air}}}{n_{\text{sapph}}}\right)^2\right]\sin^2\theta - \left(\dfrac{n_{\text{air}}}{n_{\text{sapph}}}\right)^2}$$

$$\beta = 1 + \frac{\left[1 + \left(\dfrac{n_{\text{CCl}_4}}{n_{\text{st}}}\right)^4\right]\sin^2\theta - \left(\dfrac{n_{\text{CCl}_4}}{n_{\text{Ge}}}\right)^2}{\left[1 + \left(\dfrac{n_{\text{CCl}_4}}{n_{\text{Ge}}}\right)^2\right]\sin^2\theta - \left(\dfrac{n_{\text{CCl}_4}}{n_{\text{Ge}}}\right)^2},$$

where A is the absorbance, n is the index of refraction, and the subscripts refer to the interfaces (sapph = sapphire, st = stearate), so that for the Ge/stearate/CCl$_4$ system (100 reflections at 45°) the monolayer absorbance at 2928 cm^{-1} = 0.4/192 or 0.4/(1.92 × 100) per reflection; i.e., for a Ge IRE giving 25

reflections at 45° the monolayer absorbance at 2928 cm^{-1} = 0.4 × 25/(1.92 × 100) = 0.052.

If an IRE is place in contact with a solution, the evanescent wave will penetrate the solution and the spectrum of the solution will be obtained in addition to the spectrum of any solute which might be adsorbed on the IRE. However, the solutions used were dilute ones, and it is estimated that the amount of dissolved stearic acid in a 10^{-3} M solution sampled by the evanescent wave was equivalent to about 2–5% of a monolayer of adsorbed acid. This estimate, based on the penetration depths to be expected with the geometries of the IREs used (9), is supported by internal reflection spectra of dilute solutions, to be described elsewhere, which showed that the solute could no longer be detected in solutions weaker than about 10^{-3} M. The absorption of dissolved adsorbate was consequently negligible.

RESULTS

ADSORPTION AND DESORPTION

The adsorption of stearic acid onto various IREs was studied using the Beckman IR-12. For example, after the background spectrum of a clean Ge IRE had been recorded (A, Fig. 2), a 1.4 × 10^{-4} M solution of stearic acid in CCl$_4$ was placed in the cell and a series of spectra was recorded after various times had elapsed. Trace B of Fig. 2 shows the results obtained after 16 hr of adsorption, with A_{2928} = 0.0142. If A_{2928} for monolayer coverage under these conditions is taken as 0.052, then the coverage indicated by spectrum B of Fig. 2 is about 0.2 monolayer. Similar results were obtained with solutions of higher concentrations, the amount adsorbed not increasing significantly as the concentration was increased to 10^{-2} M, implying that a maximum or equilibrium value had been reached. The stearic acid solution was then replaced by CCl$_4$, and the desorption of stearic acid was followed by monitoring the decline in A_{2928}. The amount of residual stearic acid was about 16% of a monolayer after a period of five days.

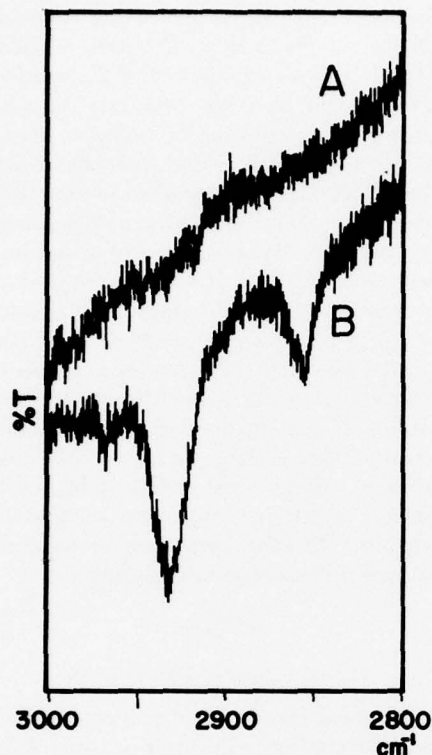Other experiments were carried out with

FIG. 2. Adsorption of stearic acid on Ge. Spectra were recorded with the Beckman IR-12, using a Ge IRE giving 25 reflections at 45°. A: background. B: after 16 hr in 1.4×10^{-4} M stearic acid solution. The ordinates are displaced.

single-beam spectra such as A, B, and C were stored by the instrument's digital computer and could be recalled at will so that ratioing and scale expansions could be carried out. The ratio of spectra A and B resulted in spectrum D, showing only the bands of CCl_4 (13). The solvent bands, which were not intense but might overlap those of the solute or adsorbed material, could be removed by ratioing a "sample spectrum" such as C against spectrum B, yielding a trace such as F. A spectrum such as B was recorded for any one experiment and

alumina (Fig. 3) and PdO-coated Ge IREs (Fig. 4), and adsorbed stearic acid was detected.

Similar adsorption experiments were carried out with the Fourier transform spectrometer, using the device shown in Fig. 1; some results are shown in Fig. 5. After a clean Ge IRE had been installed in the device, a spectrum (A) was recorded. The resolution was chosen to be 8 cm⁻¹, constant over the entire frequency range, because little would be gained by using better resolutions. The cell was then filled with CCl_4, and the background spectrum B was obtained, now showing a CCl_4 band. Stearic acid solution was then introduced and additional spectra were recorded, e.g., trace C. All

FIG. 3. Stearic acid adsorbed on (0001) α-Al_2O_3. Spectra were recorded with the Beckman IR-12, using an IRE of α-Al_2O_3 which was cut to expose (0001) faces, and which yielded 100 reflections at 45°. Spectra were recorded with the IRE in air, subsequent to adsorption of stearic acid from 1×10^{-2} M solution; see text (16). A: unpolarized. B: parallel polarized. C: perpendicular polarized. The ordinates are displaced.
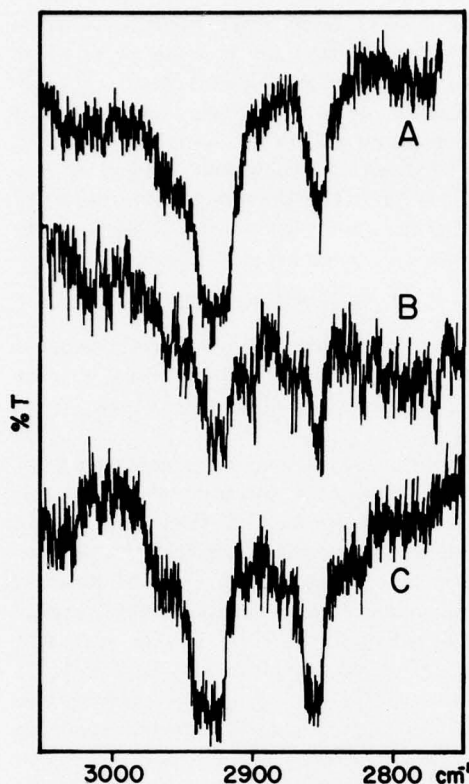
FIG. 4. Stearic acid adsorbed on PdO/Ge. Spectra were recorded with the Beckman IR-12, using a Ge IRE one side of which had been coated with a thin film of PdO. After adsorption had been completed from 10^{-3} M solution, unpolarized (A), parallel (B), and perpendicular (C) polarized spectra were recorded. The ordinates are displaced.

used as background spectrum for all subsequently recorded "sample spectra" so that a series such as spectra E–H resulted. Both single-beam and ratioed spectra of Fig. 6 exhibit certain features which are not directly pertinent (13). It was possible to scale-expand each spectrum, or segments of it, at will; some examples are shown in Fig. 6.

Experiments were carried out with solutions varying from 6.2×10^{-5} to 1.2×10^{-3} M. At the lowest concentration the adsorption process, determined by the increase of A_{2928}, required several hours for completion. The spec-

tra were fairly noisy, e.g., A, Fig. 6, but the main spectral features of adsorbed stearic acid were discernible. For trace A of Fig. 6, A_{2928} $=0.011$ equivalent to about 6% of a compressed stearic acid monolayer. The lowest coverage detected with a 6.2×10^{-5} M solution was about 3% of a monolayer, and was observed about 10 min after contacting the IRE with the solution, with a signal-to-noise ratio of about 2. The quality of the spectra was better at higher coverages, e.g., B, Fig. 6, equal to about 0.3 monolayer. Also, the rela-
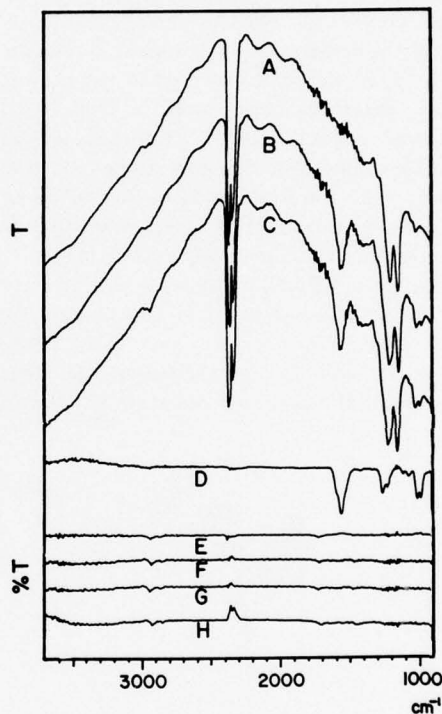
FIG. 5. Stearic acid adsorbed on Ge. Spectra were recorded with the Digilab FTS-14 Fourier transform spectrometer, using a Ge IRE ($50 \times 20 \times 1$ mm, $30°$ bevel angles, yielding about 90 reflections). A: Ge IRE in air. B: Ge IRE in CCl_4. C: Ge IRE after immersion in 1×10^{-4} M stearic acid solution for 30 min. D: ratio of spectra A and B. E–H: ratios of spectrum B with other spectra such as C recorded after the following times of immersion in minutes: E, 10; F, 30; G, 120; H, 720. The ordinates are displaced (13). All spectra were recorded with 400 scans at a resolution of 8 cm^{-1} constant over the spectral range shown.

tively weak carbonyl band (C, D, Fig. 6), and the weak methylene bending band at 1455 cm^{-1} could be observed (E, Fig. 6). When desired, the spectra could be smoothed (14). Absorbances were obtained from the computer readout and the plots (15).

ORIENTATION OF ADSORBED SPECIES

The "wagging bands" or band progressions (a series of bands caused by interactions between methylene groups when long-chain hydrocarbons are symmetrically arranged) which were previously used to infer information about the orientation of adsorbed carboxylic acids (7, 8) were not observed in the present study; either the bands were too weak to be observed or not present. However, it was possible to obtain some information about the stearic acid adsorbed on IREs by means of polarized radiation. Such effects have already been demonstrated in another study (11).

The electric field amplitudes at the interface (9, 11) of the Ge/stearic acid/CCl$_4$ system are $E_x = 1.397$, $E_y = 1.520$, and $E_z = 1.546$, where E_x and E_z are the amplitude components of the polarized radiation parallel to

the incident beam which forms a 45° angle with the interface, and E_y is the amplitude of the perpendicular polarized beam. The absorbance ratio for stearic acid molecules oriented normal to the interface is $A_\perp/A_{||} = 1.183$, and for completely random orientation is 0.532 (11). Moreover, for the case where all of the adsorbed molecules lie flatly on the surface, the expected absorbance ratio is,

$$A_\perp/A_{||} = \tfrac{1}{2}E_y^2/(\tfrac{1}{2}E_x^2 + \tfrac{1}{2}E_z^2) = 0.343.$$

It is thus possible to obtain some information about the adsorbed acid molecules by comparing the expected and measured $A_\perp/A_{||}$ values.

Some $A_\perp/A_{||}$ measurements were carried out. For example, the spectrum of stearic acid adsorbed onto a Ge IRE from 9.3×10^{-3} M solution was measured, and then the measurement was repeated using parallel polarized radiation and again using perpendicular polarized radiation (all three spectra were very similar to spectrum B of Fig. 2). The $A_\perp/A_{||}$ ratio at 2928 cm^{-1} was 0.526, implying that the adsorbed molecules were oriented randomly on the Ge surface.

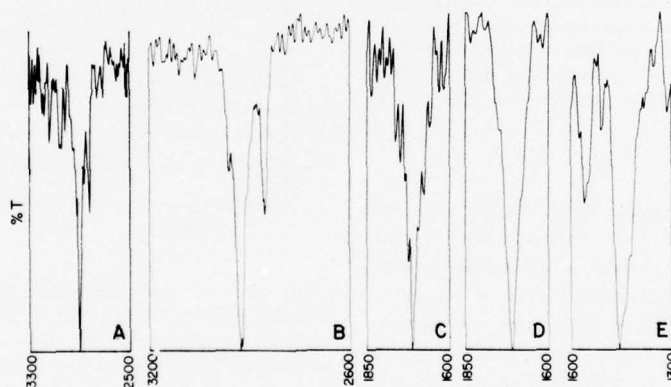Similar experiments were carried out with

FIG. 6. Stearic acid adsorbed on Ge. Segments of ratioed spectra recorded with the Digilab FTS-14 Fourier transform spectrometer (see legend of Fig. 5, and text) (13, 14). A: after 19 hr immersion in 6×10^{-5} M stearic acid solution; 400 scans, smoothed (14). B: after about 2 min immersion in 1×10^{-3} M stearic acid solution; 300 scans, not smoothed. C: after 10 min immersion in 1×10^{-4} M stearic acid solution; 400 scans, not smoothed; this is a small segment of E, Fig. 5. D: spectrum C, after smoothing (14). E: after 7 hr immersion in 1×10^{-4} M stearic acid solution; 400 scans, smoothed (14); this is a small segment of H, Fig. 5. All spectra were recorded at 8 cm^{-1} resolution.

stearic acid adsorbed from 1×10^{-2} M solution onto an α-Al_2O_3 IRE fabricated to expose (0001) surfaces (11). The alumina IRE gave 100 reflections at 45° and this, along with poor matching of refractive indices (9), caused all of the radiation to be absorbed by the solution, so that it was not possible to study the adsorbed film *in situ*. Consequently, after equilibrium adsorption had occurred, the IRE was removed from the stearic acid solution and dipped several times into CCl_4 in order to remove adhering solution (16). Spectra were then recorded with the IRE in air (Fig. 3), the A_{2928} value obtained from spectrum A indicating that an amount of stearic acid equivalent to a compressed monolayer was on the plate. The $A_\perp/A_{\parallel}$ value obtained from spectra B and C of Fig. 3 was 1.62. The $A_\perp/A_{\parallel}$ ratios for this system for the two extreme orientations are 1.28 for completely random orientation and 2.13 for ideally close-packed, normal orientation of the adsorbed stearic acid. The observed value of 1.62 suggests that the adsorbed film was partially oriented (16). An *in situ* study of the Al_2O_3/stearic acid/CCl_4 system is possible if a properly shaped IRE is available, i.e., one permitting an angle of incidence greater than 60°, the critical angle for the system being close to 60°.

Far greater polarization effects were found with the Ge/PdO/stearic acid/CCl_4 system (Fig. 4), implying that the adsorbed layer on the PdO portion of the surface was relatively highly oriented. However, the spectra are relatively poor and because the actual nature of the surface is not known, A_{2928} and $A_\perp/A_{\parallel}$ values and their significance are uncertain: unlike the oxide coating on the Ge IRE's, the PdO is not optically thin, so that the changes in polarization may be partly or wholly brought about because of differences in indeces of refraction.

KINETICS

It is well known that the intensity changes of one absorption band can be followed with a conventional dispersion spectrometer by disengaging the instrument's scanning drive; the
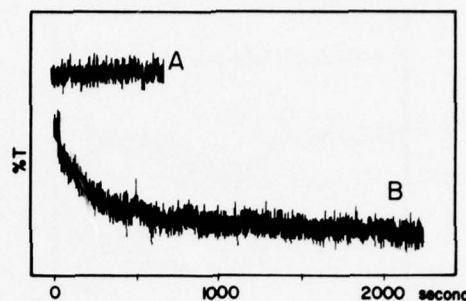

FIG. 7. Kinetics of adsorption of stearic acid on Ge. The Beckman IR-12 was set and remained at 2928 cm^{-1}, and the background trace A was recorded. The Ge IRE (25 reflections at 45°) was then immersed in 1.4×10^{-4} M stearic acid solution and trace B was recorded. The ordinates are displaced.

instrument is set at one particular frequency, and intensity changes occurring at that frequency are recorded as a function of time. Such measurements were possible with the present system, and Fig. 7 shows the 2928 cm^{-1} band of stearic acid changing with time.

It is not possible to carry out identical measurements with the FTS-14, because a Fourier transform spectrometer always "scans" all frequencies simultaneously. However, the instrument's operation is rapid enough to permit measuring series of spectra covering the instrument's entire spectral range. Such series of spectra, e.g., E–H, Fig. 5, can then be used to follow the intensity changes of many different bands, e.g., Fig. 8.

It is thus possible to obtain information about adsorption from solution either by monitoring a single band or, preferably, by monitoring the intensity changes of many bands so that composition changes of the adsorbed layer can also be followed, and this is done by direct measurements of the rate of build-up of the adsorbate on the surface. Mass transport influences can be determined by varying the circulation of the solution in the usual way. In the present case, the rates are not meaningful because the solutions were not stirred, although the effects of diffusion as rate-controlling process can be estimated (17).
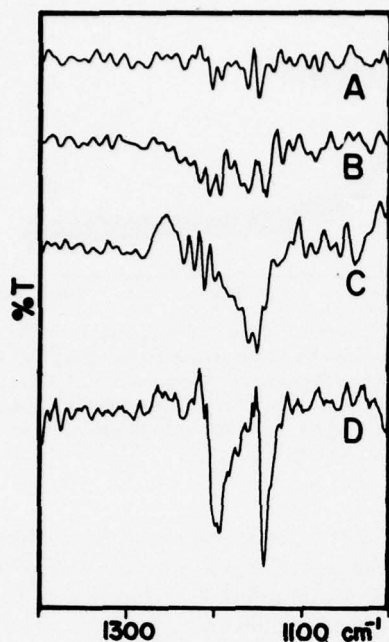
FIG. 8. Kinetics. Segments of spectra recorded with the Digilab FTS-14 Fourier transform spectrometer, taken from a series shown in part as E–H, Fig. 5; see legend of Fig. 5. The ordinates are displaced. The time in minutes after immersion were: A, 2–3; B, 30; C, 110; D, 990.

ISOTHERMS

It seems feasible to measure adsorption isotherms by following intensity changes, say A_{2928}, as function of solution concentration and, with proper thermostating, to observe the effects of temperature. This was not attempted in the present study; solution concentration were varied at random, and the IRE used was cleaned after an experiment with a particular solution was completed. The equilibrium amounts of stearic acid adsorbed on Ge IREs were about 6% of a compressed monolayer with a solution of 6.2×10^{-5} M, about 9% with 1×10^{-4} M, about 22% with 6.2×10^{-4} M, and 25–31% with solutions in the 10^{-3}–10^{-2} M range, suggesting that the room-temperature isotherm rose steeply and flattened out at concentrations above about 10^{-4} M.

DISCUSSION

THE Ge/STEARIC ACID/CCl₄ SYSTEM

The present results indicate that stearic acid was rapidly taken up from the unstirred solutions by the surface of the Ge IREs, the adsorption being complete in about 10 min. at concentrations above 10^{-4} M. There were no changes in the spectra when the adsorbed films were allowed to remain in contact with the solutions for periods up to 20 hours; and it is particularly interesting to note that the carbonyl band was observed at 1713 cm⁻¹, close to the frequency of bulk stearic acid, and that its intensity did not change, no new bands were observed and, judging from the results with polarized radiation, the adsorbed layer exhibited no orientation. In contrast, Sharpe (18) reported the carbonyl stretching of an oriented stearic acid monolayer deposited on a Ge IRE to absorb at 1745 cm⁻¹, and attributed that to a relatively unbonded acid carbonyl absorption unperturbed by the hydrogen bonding interactions found with bulk stearic acid. Also, when the oriented layer remained on the Ge IRE for a few hours, a new band appeared near 1593 cm⁻¹, probably indicating the formation of a Ge salt by chemisorption (18). It thus appears that rather different results are obtained if the acid is adsorbed from CCl₄ solution: the adsorbed layer was irregular (indicated by polarization effects); consisted of randomly oriented, hydrogen-bonded dimers and/or polymers (indicated by the similarity of the carbonyl absorptions of the adsorbed layer and of bulk acid); and did not react with the surface in a reasonable time, probably because the intermolecular bonding prevented or greatly slowed down the reaction of acid with the Ge surface. However, it is uncertain if a direct comparison is valid, because Sharpe did not mention how his Ge was cleaned.

Monolayers of long-chain fatty acids are formed by adsorption from solution onto metal oxides (19–21) and some catalysts (22), while only fractional coverage is achieved with carbon and silica (23–26). It is therefore tempting

to class the Ge IRE surface with carbon and silica, and to attribute the low surface coverage achieved with Ge to "polarity effects." However, until structural information about other adsorbed films is obtained, comparisions would seem premature.

Ge/CCl₄ Reaction

Bands were observed at 1200 and 1150 cm^{-1} when Ge IREs were exposed to CCl₄ or solutions of stearic acid in CCl₄. The band's intensities increased with time and changed relative to one another, e.g., Fig. 8. The unknown material causing the bands was tenaciously held to the IREs, could not be removed the chromic acid, and appears to have its origin in a slow reaction between CCl₄ and Ge.

The Internal Reflection Method

As the present exploratory experiments have shown, it is feasible to use infrared internal reflection techniques to obtain direct information about "adsorption from solution." Extrapolating the present results, it should be possible to study a variety of adsorbent–adsorbate systems and obtain, with a single experimental technique, much of the information of interest, i.e., adsorption and desorption kinetics, adsorption isotherms, perturbation of the adsorbate and of the surface species present on the adsorbent's surface, orientation or structural information about the adsorbed molecules, diffusion, and chemisorption. However, although the method seems an attractive one, several points must be kept in mind: (a) Obviously, the method is restricted to solids which can be fashioned to form IREs. Although single crystals of suitable size are becoming more readily available, the choice of adsorbent cannot be a wide one at present. Limiting the method to the use of Ge or Si IREs, the materials which are not only readily available but also optically the most suitable, would be somewhat restrictive. However, it may be possible to develop Ge or Si IREs coated with a very thin film of adsorbent, although this might lead to optical difficulties

of the type discussed by Srinivasan and Kuwana (27); (b) The optical properties of the IRE, solute, and solvent must be such that there is only weak coupling between IRE and solvent. The concepts involving an IRE bearing a film much thinner than a penetration depth have been considered by Harrick (9); (c) If the concentration of the solution is high, the spectrum will show the absorption bands of the dissolved as well as the adsorbed solute and overlapping of bands may result; if extinction coefficients are known, a correction can be applied if the measurements are precise enough; (d) The "sample" is small in all cases; and, although multiple reflections are used, absorptions are small. Consequently, absorbance of 0.4 of a compressed monolayer of calcium stearate deposited on a sapphire surface was used (4); the sapphire plate gave 100 reflections at 45°. A conversion from the sapphire system to the germanium system is possible, and smaller numbers of reflections may be used. In all cases, however, relatively great demands are placed on the instrumentation. In general, however, judging from the IR-12 results, it would appear that good results can be obtained with a research-quality dispersion spectrometer, although in general better results can be obtained with the FTS-14 Fourier transform spectrometer (28).

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13. The single-beam spectra A, B, C of Fig. 5 are characteristic of the emission of the instrument's source modified by the beamsplitter characteristics, mirror reflectances, and the like, as well as by the absorption characteristics of the Ge IRE. The bands below 1500 cm^{-1} are Ge absorptions. The prominent 2400–2300 cm^{-1} bands are due to atmospheric CO_2. The "noise" in the 1800–1400 cm^{-1} region is due to atmospheric H_2O not removed by flushing. The ratioed spectra D–G are noisier above 3000 cm^{-1} and below 2500 cm^{-1} than in the centers of the spectra because relatively small numbers are ratioed. The spectra are generally flat but small changes in flushing, temperature, and sample positioning can lead to variations. This is particularly noticeable in spectrum H, where a large negative CO_2 band indicates that the flushing conditions had changed. However, unless there is overlapping with absorption bands of the sample, such background variations are not important.

14. The FTS-14 system can be used to smooth a spectrum, and the results are analogous to the frequently applied practice of manually running a judiciously placed single line through the middle of a noise band of a noisy spectrum. With the FTS-14, the spectrum is in digital form, and the computer averages predetermined numbers of data points and plots out average values, to yield a smoothed spectrum.

15. The FTS-14 system prints out maximum and minimum Y values ($Y = T$, $\frac{c}{c}T$, etc.) for a spectrum or any segment of it, and these values along with the plotted spectrum were used to compute absorbances. For example, for part A of Fig. 6, the maximum and minimum values were 0.988 and 0.956, respectively, the plot's ordinate being precisely 10 inches. The maximum value included the noise. The base line for the 2928-cm^{-1} band was estimated to fall about 1.5 inches below the top of the plot; i.e., the maximum of the 2928-cm^{-1} band was taken as 0.981, which value was used to compute $A_{2928} = 0.0259$.

16. The dipping procedure is an unsatisfactory one, although acceptable for the present exploratory experiments, because it is not certain that the adsorbed layer remains undisturbed. It is possible that desorption and readsorption occur and the orientation of the film be changed. On the basis of previous work, for example, it would be expected that the adsorbed layer would be highly oriented (11).

17. The rates, e.g., Fig. 7, are not meaningful. By solving the diffusion equation with pertinent boundary conditions and assuming the diffusion coefficient of stearic acid to be 10^{-5} cm^2/sec, the amount of material which could have diffused at $t = 17$ min (Fig. 7) was about 100 times the maximum amount of stearic acid which was found to be adsorbed. In other words, the rate measured was not entirely the rate of diffusion, but diffusion definitely was the limiting process at the beginning of the adsorption process.

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28. The optical advantages of the Fourier transform spectrometer vis-à-vis the dispersion spectrometer need not be belabored, and the advantages of data handling by digital computation using the spectrometer's computer are obvious. However, as is almost always the case, a direct comparison of the dispersion and Fourier transform spectrometers was not possible. For example, the FTS-14 yielded a spectrum covering the 3900–400 cm^{-1} region with a resolution of 8 cm^{-1} constant over the entire region in a period of about 5 min, while the IR-12 would need 2 to 3 hr to cover the same spectral region but with varying resolution. The FTS-14's operation cannot be slowed to match the IR-12's operation, and high-speed operation causes the IR-12 to produce a completely meaningless trace. Also, different IRE attachments were used.

Infrared Study of Adsorption *in situ* at the Liquid–Solid Interface [1]

V. Adsorption of Octadecanol, Octadecylamine, and Octadecanedioic Acid on Silica, and a Criterion for Considering Competitive Adsorption

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Infrared spectra were recorded *in situ* of octadecanol (A), octadecylamine (B), and octadecanedioic acid (C) adsorbed from CCl_4 solutions onto highly degassed silica. Adsorbed A interacted with silanols and caused a shift, $\Delta\nu_{OH}$, of the silanol band of ~ 275 cm^{-1}; the data suggest that A dimers interacted with silanols but also adsorbed without such an interaction. B interacted extensively and strongly with silanols, causing a $\Delta\nu_{OH} \sim 750$ cm^{-1}. Also, some B was chemisorbed. In contrast, C adsorption was slight and the interaction with silanols weak; apparently some C polymer chains were broken. As interactions with silanols cause a perturbation of the silanol band and the extent of the perturbation is a measure of the strength of the adsorption, it may be possible to use $\Delta\nu_{OH}$ as criterion in considering competitive adsorption processes occurring on hydroxylated surfaces.

INTRODUCTION

Recently a new infrared method for studying adsorption *in situ* at the liquid–solid interface was developed (1–4) so that adsorption from solution could be studied under well-defined conditions. The adsorptions of aniline of silica, stearic acid on zinc oxide, silica, and alumina, of decanoic acid on magnesia, and of stearic acid on germanium internal reflection elements were examined and information about the nature of the adsorbed species was obtained. In some cases the infrared spectra also provided some information about the orientation of the molecules within the adsorbed layer. As the technique had shown itself to be a useful one, we have continued the studies and have examined the adsorption of octadecanol, octadecylamine, and octadecanedioic acid on silica with the intent of providing some information about the effect of terminal functional groups on the adsorption of linear C_{18} molecules.

[1] Part IV: Ref. (4).

EXPERIMENTAL

The experimental procedures used have been described in detail elsewhere (3). Octadecanol and octadecylamine (5) were purified by vacuum sublimation; octadecanedioic acid of $>99\%$ purity (6) was used as received. The Cab-O-Sil (7) silica pellets (3) were air-leached at 700°C for 6 hr and degassed for 6 hr at 800°C.

RESULTS AND DISCUSSION

As observed earlier, the principal feature of the spectrum of a degassed silica sample was the sharp 3745 cm^{-1} band of free silanol groups of the silica surface (spectrum A, Fig. 1). When the sample was immersed in CCl_4 or in any of the solutions employed, the transmittance increased because the scattering of radiation by the sample was decreased, and the silanol band shifted to 3685 cm^{-1}, e.g., Spectrum B, Fig. 1. In addition to these general effects, the perturbation of the silanol

band and the bands of adsorbed material were observed, in the manner described previously (1–4).

Octadecanol

When a degassed silica sample was immersed in CCl_4 and then the pure solvent was replaced with solutions of octadecanol in CCl_4, changes were observed in the O–H and C–H regions of spectra (Fig. 1). As the adsorption proceeded, a pair of bands at 2922 and 2850 cm^{-1} became progressively more intense. These bands, which match bands at 2922 and 2850 cm^{-1} of octadecanol dissolved in CCl_4, are attributed to the C–H stretching modes of adsorbed octadecanol. Also, a broad absorption appeared in the 3700–2000 cm^{-1} range, and the Si–OH band was slightly perturbed (B–H, Fig. 1). Some tailing appeared on the low frequency side of the Si–OH band; the latter's intensity was not markedly affected, but it is difficult to detect small changes in band heights because of the Si–OH band's great intensity. The broad absorption was caused by two overlapping bands centering near 3470 and 3330 cm^{-1}. No bands were observed below 2000 cm^{-1}. When the adsorbate solution was replaced with pure CCl_4 solvent, there were no changes in band intensities which would indicate that some desorption had occurred.

The difference in frequencies of the unperturbed Si–OH band and the broad 3470 cm band, $\Delta\nu_{OH}$, is approximately 275 cm^{-1} (a precise value cannot be obtained because of the broadness of one band), and is of the order of magnitude expected of $\Delta\nu_{OH}$ for the perturbation of a surface hydroxyl by interaction with the OH functional group of an alcohol absorbate (8–11). Consequently, the 3470 cm^{-1} band is attributed to surface Si–OH groups perturbed through interaction with the hydroxyls of the adsorbed alcohol. The second broad band is attributed to the perturbed $\nu(O–H)$ mode of the adsorbed alcohol itself.

The $\nu(OH)$ band of the alcohol is a broad one centering near 3357 cm^{-1} and is consider-
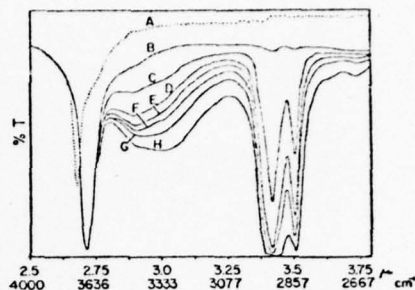
FIG. 1. Octadecanol adsorption. After the spectrum A of the degassed sample *in vacuo* was recorded, the sample was immersed in CCl_4(B). A 0.5 mM octadecanol solution was then introduced and circulated, and spectra were recorded after 0.5 hr (C), 12 hr (D), and 36 hr (E). A 1 mM octadecanol solution was then introduced and circulated, spectrum F being recorded after 3.5 hr and spectrum G after 20 hr. Spectrum H was recorded 3.5 hr after a 5 mM solution had been introduced.

ably lower than the frequency near 3600 cm^{-1} expected for a free O–H stretching (12, 13), so that it seems probable that the alcohol existed in an associated form in CCl_4 solution. The band center of the second broad band bought about by adsorbed octadecanol is close to the band center of the dissolved octadecanol, suggesting that what has been termed the 3303 cm^{-1} band was caused by adsorbed, associated octadecanol molecules subjected to some additional perturbation because of interactions with the surface. The overall results thus suggest that the uptake of octadecanol by the silica involved the binding of octadecanol dimers to surface Si–OH groups via interactions of the alcohol hydroxyls and silanols, the hydrocarbon chains being "parallel" to the surface as the Claesson's model (14). With such an orientation, the adsorbed molecules being presumably randomly distributed, the establishment of cooperative vibrations resulting in "wagging bands" or band progressions of the type found in well-structured aggregates of normal higher alcohols (15) would not be possible.

In a study of the adsorption of aliphatic alcohols from CCl_4 onto nonporous silica it was found that the amount of methanol adsorbed
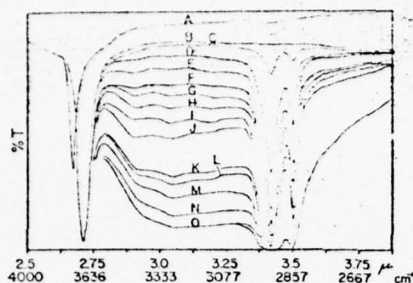
FIG. 2. Octadecylamine sorption. A: degassed sample in vacuum; B, after immersion in CCl₄. Spectra were recorded after 0.1 mM octadecylamine solution had been circulated for the following periods in hr: C, 0.5; D, 20; E, 62. The solution was replaced with 0.2 mM solution, and spectra were recorded after F, 3.5; G, 18; H, 42; I, 66, and J, 120 hr. The solution was replaced by 0.3 mM solution, and spectra were recorded after 4.5 (K) and 144 (L) hr. M was recorded 19 hr, and N after 96 hr, after 0.4 mM had been circulated. Spectrum O was recorded 90 hr after 0.5 mM solution had been circulated.

per unit area of adsorbent surface varied markedly with the degree of hydroxylation of the surface. With higher members of the homologous series the effect was lessened, and occurred only at very low concentrations with *n*-octanol, suggesting that the adsorption of methanol depended mainly on the interaction of methanol hydroxyls with surface silanols, whereas octanol molecules were adsorbed mainly because the hydrocarbon chains were held to the surface (16). The present data also point to such an effect. Judging from the intensities of the C–H bands, the amount of octadecanol adsorbed was fairly large, but the perturbation of the Si-OH band was fairly small. Also, at low coverage (C, Fig. 1) the 3470 cm⁻¹ band of perturbed silanols was relatively intense, while at high coverage (E, Fig. 1) the 3330 cm⁻¹ band was the more prominent. The effects suggest that although some Si-OH -alcohol interaction occurred throughout the adsorption process, the relative extent of that interaction diminished with increasing coverage so that at high coverage a large fraction of octadecanol molecules adsorbed without interacting with silanols.

Octadecylamine

The main effects observed when silica was immersed in octadecylamine solutions (Fig. 2) were as follows. (a) The C–H bands at 2922 and 2850 cm⁻¹ of adsorbed octadecylamine grew progressively. (b) The Si–OH band broadened, declined slightly in intensity, and shifted to 3682 cm⁻¹. (c) A broad and intense absorption appeared over the 3700–2200 cm⁻¹ region. Superimposed on the broad absorption were three minor absorptions centered near 3440, 3280, and 3137 cm⁻¹. The overall effects were thus identical with those found on exposing silica to gaseous NH₃ (17), aniline (18) and aliphatic amines (19), i.e., the amine interacted strongly with and perturbed the surface silanols. In the present case, the broad absorption appears to center near 2950 cm⁻¹, implying a $\Delta\nu_{OH}$ of about 800 cm⁻¹. Such a high value would be expected for the strong amine-silanol interaction; for NH₃, $\Delta\nu_{OH} = 750$ cm⁻¹; and for various amines, $\Delta\nu_{OH} = 840$–950 cm⁻¹ (19).

The three minor absorptions in the N–H range cannot be assigned with certainty. One of the bands is at higher frequency than the 3392 cm⁻¹ ν_a(N–H) or the ν_s(N–H) band of octadecylamine in CCl₄; and the other two bands are at lower frequencies than would be expected for the ν(N–H) octadecylamine bands
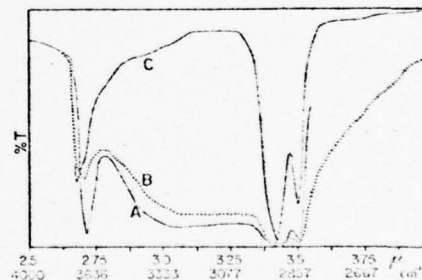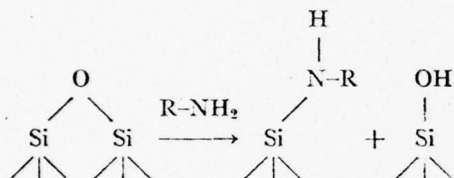

FIG. 3. Octadecylamine desorption. After spectrum O of Fig. 2 has been recorded, the solution was replaced by CCl₄ and after 24 hr, spectrum A was recorded. The CCl₄ was removed, the system degassed for 14 hr at 25°C and spectrum B was recorded. Then, after degassing at 200°C for 4 hr, spectrum C was recorded.

shifted to lower frequencies because of hydrogen bonding, and their frequencies do not fit Bellamy and Williams relation between ν_a(N–H) and ν_s(N–H) (20) although unsymmetrical loading, i.e., hydrogen bonding to only one of the hydrogen atoms of the amine group, may have caused a larger shift for the ν_s(N–H) than for the ν_a(N–H) mode (21). Also, when the sample was mildly degassed, the 3137 cm^{-1} band disappeared (C, Fig. 3). Consequently, it is probable that three distinct surface species were formed in addition to the physically adsorbed amine. One of these might be a secondary amine structure (absorbing at 3440 cm^{-1}) formed by a reaction,

$$
\begin{array}{ccccc}
& & & & H \\
& & & & | \\
O & & & N\text{--}R & OH \\
/ \ \ \backslash & & R\text{--}NH_2 & / \ \ \backslash & | \\
Si & Si & \longrightarrow & Si & + \ Si \ . \\
/|\backslash & /|\backslash & & /|\backslash & /|\backslash
\end{array}
$$

A similar structure was postulated to account for a band at 3435 cm^{-1} found upon adsorbing aniline on silica (18). Some support for such a hydroxyl-generating chemisorption comes from the observation that the Si–OH band was broadened and exhibited tailing after much of the physically adsorbed amine had been removed (C, Fig. 3). Perhaps such a reaction can account for the chemisorption effects noted on adsorbing octadecylamine onto silica from
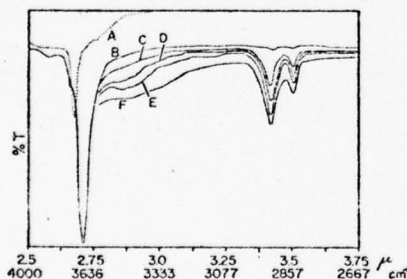
FIG. 4. Octadecanedioic acid sorption. Degassed sample *in vacuo* (A) and after immersion in CCl₄ (B). Spectra were then recorded after the circulation of a solution ~0.03 mM for 42 hr (C), ~0.06 mM for 48 hr (D), ~0.1 mM for 48 hr (E), and ~0.03 mM for 4 hr (F).

xylene (22). In the absence of more detailed spectroscopic data, however, the nature of the species remains uncertain.

Octadecanedioic Acid

The spectra recorded of silica immersed in octadecanedioic acid solutions show that the adsorption was slow and sparse, the C–H bands of the adsorbed acid (2925, 2857 cm^{-1}) growing only slowly and not reaching great intensities (Fig. 4). The Si–OH band was only slightly perturbed. However, a weak, broad band appeared near 3500 cm^{-1} (D, Fig. 4), and another broad absorption or tailing (termed the 3200 cm^{-1} band in analogy to a similar band observed with stearic acid–silica) extended to near 2600 cm^{-1}.

Similar changes were obtained when stearic acid adsorbed on silica (3) and, using the assignments, and reasons for them, made earlier (3), the 3500 cm^{-1} band is attributed to ν(O–H) of individual carbonxyl groups interacting with silanols, while the broad 3200 cm^{-1} band is attributed to the ν(O–H) mode of dimerized carboxyl groups. The stearic acid–silica and octadecanedioic acid–silica systems thus behave similarly. In the latter system, however, the interaction of an individual carboxyl group, i.e., one not associated with another carboxyl group, with a silanol does not necessarily imply that the adsorbed species is monomeric, as is the case with stearic acid, but only that some of the di-acid polymer chains were broken to yield terminal carboxyls which could then interact with silanols. The length or configuration of the chains bearing such carbonxyls are unknown; presumably the polymer is lying "flat" on the surface. Probably the adsorption was slower and less copious than that of stearic acid because the polymer chains had to be disrupted so that carboxyl–silanol interactions could take place.

Competitive Adsorption

The present studies of "adsorption from solution" are intended to provide some information about adsorbed species, in analogy

to similar spectroscopic studies carried out with gas–solid systems. Preferential of "selective" adsorptions are involved. However, it is obvious that the systems are not simple because two adsorbates are always involved and their competitive adsorption influences adsorption rates and the nature of the adsorbed layer. The complexities involved in competitive adsorption have been reviewed in Kipling's monograph (23), and factors such as the polarity of the surface or heats of immersion have been considered. In particular, many workers have stressed the importance of adsorbate-hydroxyl interactions for adsorption onto hydroxylated surfaces. For such cases, the perturbation of surface hydroxyls might constitute a useful criterion for considering competitive adsorption.

Spectroscopic studies of gas-solid interactions have provided numerous examples of the perturbation of surface hydroxyls by adsorbed materials of all types (24), and it seems generally accepted that the extent of the perturbation, in terms of the magnitude of the hydroxyl shift $\Delta\nu_{OH}$, is a measure of the strength of the OH–adsorbate interaction. The mechanism is still in question, but it is clear that the magnitude of $\Delta\nu_{OH}$ is related to the group functionality of the adsorbate in most cases (25). Similar hydroxyl shifts occur when hydroxylated solids are immersed in liquids, e.g., Fig. 1, although data are sparse and some of them were obtained in the overtone region (26). It seems useful to extend these concepts to adsorption onto a hydroxylated surface from a binary solution.
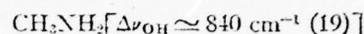
For example, for the methyl acetate/benzene/silica gel system, methyl acetate was preferentially adsorbed (27). For benzene vapor adsorben on silica, $\Delta\nu_{OH} = 120$ cm^{-1} (25), and $\Delta\nu_{OH}$ for methyl acetate can be taken to be closely approximated by the value of 280 cm^{-1} found for ethyl acetate (25).

Also, silica adsorbs alcohols in preference to i-octane (28). For alcohols a $\Delta\nu_{OH}$ value of $\simeq 300$ cm^{-1} may be taken; for i-octane, the $\Delta\nu_{OH}$ value is approximated by that of 45 cm^{-1} for i-heptane (25).

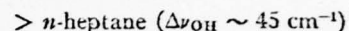Silica adsorbs alcohols ($\Delta\nu_{OH} \simeq 300$ cm^{-1}) in preference to benzene ($\Delta\nu_{OH} = 120$ cm^{-1}) (27, 29–31).

For adsorption on silica, Robert (32) reported the following preferential adsorptions:

$$CH_3NH_2[\Delta\nu_{OH} \simeq 840 \text{ cm}^{-1} (19)]$$
$$> CH_3OH(\Delta\nu_{OH} \sim 300 \text{ cm}^{-1})$$

$$(CH_3)_2CO[\Delta\nu_{OH} \simeq 330 \text{ cm}^{-1}(25)]$$
$$> (CH_3)_2CHOH(\Delta\nu_{OH} \sim 60 \text{ cm}^{-1})$$
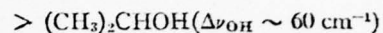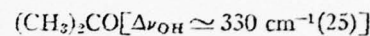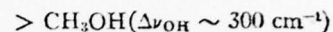
$$\text{benzene } (\Delta\nu_{OH} \simeq 120 \text{ cm}^{-1})$$
$$> n\text{-heptane } (\Delta\nu_{OH} \sim 45 \text{ cm}^{-1})$$

In each of the examples cited, the adsorbate producing the largest $\Delta\nu_{OH}$ when adsorbed individually on silica is the one which was preferentially adsorbed from a binary liquid mixture, and this lends some support to the suggestion that $\Delta\nu_{OH}$ may be used to estimate which of two, or perhaps several, components would interact preferentially with surface hydroxyls. The present data follow this trend also. However, the relation could only be expected to be a reasonable one if chemisorption were not involved, and if the adsorbate molecules were relatively simple, i.e., small ones, which would not polymerize or for which the OH-functional group interaction would not be overcome by the interaction of some other part of the adsorbed molecules with the surface.

The relation, which would be applicable to all types of hydroxylated surfaces, would seem to be a useful one which should be further explored.

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INFRARED SPECTRA OF WATER IN AQUEOUS SOLUTIONS
USING INTERNAL REFLECTION SPECTROSCOPY

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There has been a continuing interest in the structure
of water and of aqueous solutions, and many studies have em-
ployed spectroscopic techniques. These have frequently in-
volved absorption spectroscopy in the near-IR range, and
Raman scattering. In general, however, the normal IR range
has been but little used except for studies of HDO-contain-
ing solutions, and the region near 3500 cm^{-1} of the intense
H_2O absorption has been almost completely avoided. Trans-
mission techniques have been exclusively employed with ab-
sorption spectroscopy. Internal reflection spectroscopy
(IRS) techniques have been employed to examine aqueous
solutions, but the emphasis was placed on studying the
solute rather than the solvent. Also, the solute concen-
trations which had been employed in transmission studies
have been rather high. We now suggest the feasibility of
carrying out structural studies of aqueous solutions by
using IRS techniques to record spectra in the IR range, em-
ploying solutions of relatively low concentrations. For
example, the lowest concentration of aqueous HCl solution
examined by Ackermann[1] was 2.5 M by transmission techniques
in the 4000-1100 cm^{-1} range; in contrast, using IRS, the
perturbations of the O-H stretching and deformation bands
of H_2O could be observed with 0.1 M HCl.

Some of the exploratory results are shown in Figs. 1-4. Each IRs spectrum shown was "solvent-compensated" by ratioing the single-beam spectrum of the solution against the single-beam spectrum of pure H_2O, using digital computation. Spectra were recorded at room temperature, nominally 25^0C, with a modified Digilab, Inc. Model FTS-14 Fourier transform spectrometer at a resolution of 8 cm^{-1}; 200 interferograms were summed. The optics, which incorporated a Ge IRS element, were adjusted so that the transmittance near 3500 cm^{-1} was ~ 50%, i.e., the equivalent penetration depth was ~ 0.8 μ, so that quite a thin layer of liquid was studied. Some additional experimental details are given elsewhere.[2,3]

The "negative" and "positive" bands appearing in IR spectra of aqueous solutions (Fig. 1) are caused by differences between the contour of the O-H stretching band of the H_2O of the solution and that of pure H_2O, and reflect changes in the absorption of the solvent brought about by the presence of the solute. The extents of the perturbations, i.e., the intensities of the positive and negative bands and their frequencies, are functions of the nature of the solute, and can be observed at relatively low concentrations (Fig. 2). Perturbations of the H_2O deformation mode can be similarly observed (Fig.3), and quantitative relations between band intensities and solute concentrations can be obtained, e.g., Fig. 4; the upper plots refer to the variation of the absorptivity of the 3470 and 3250 cm^{-1} bands caused by NaBr, and the lower plots to changes caused by $NaNO_3$. It seems possible to interprete the effects in terms of "structure-breaking" and "structure-making" effects[4] of the solutes, but this is best deferred until computer-resolution of the bands has been effected.
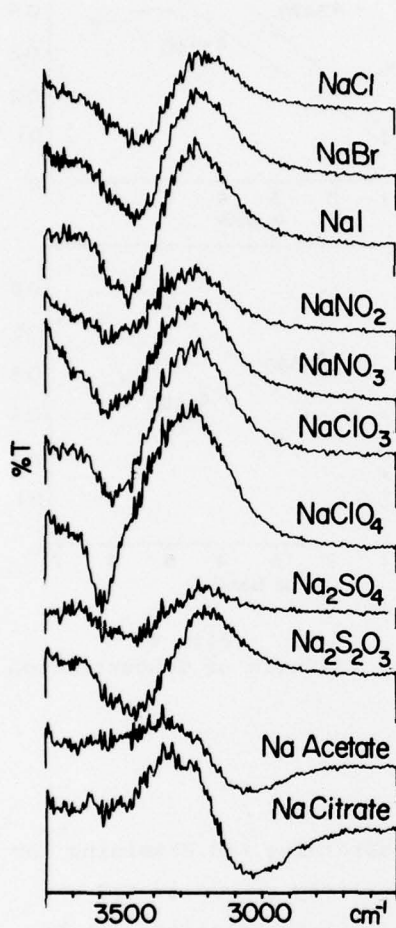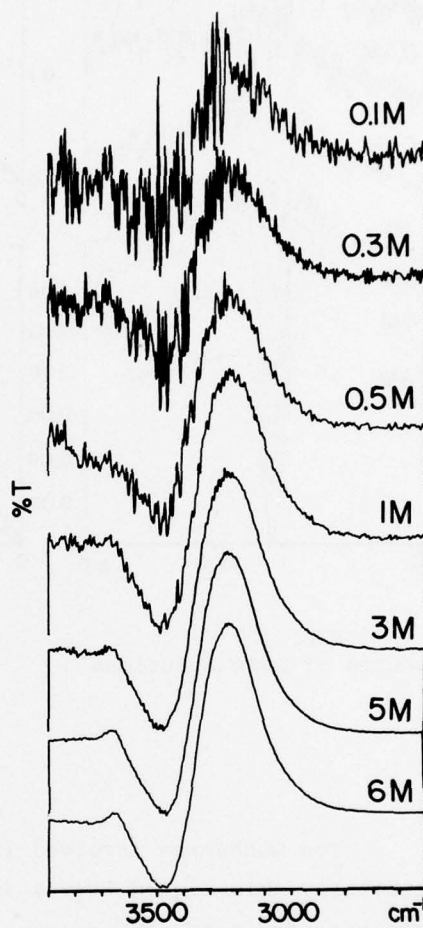
FIG. 1
Spectra of 1M Solutions
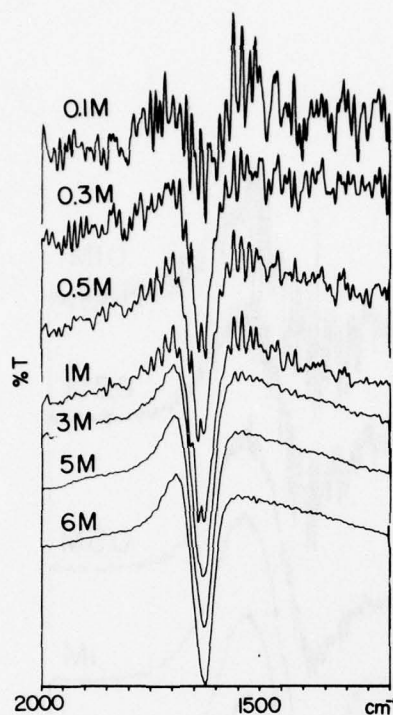
FIG. 2
Spectra of NaBr Solutions
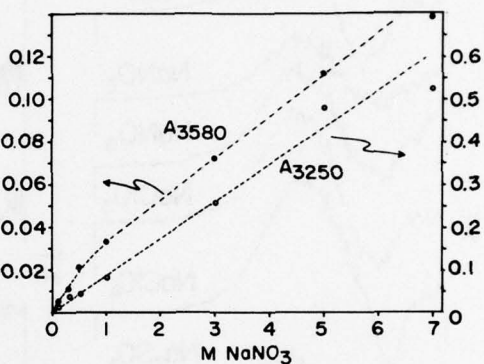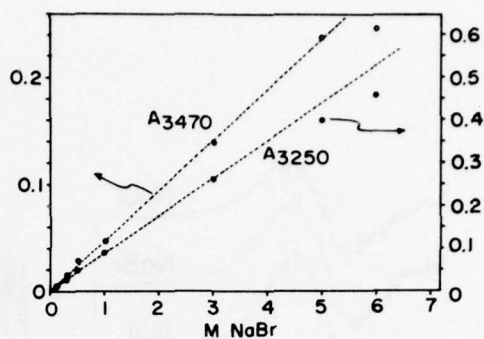
FIG. 3
Spectra of NaBr Solutions

FIG. 4
Effects of Concentration

The mechanics involved in obtaining and examining the necessarily thin liquid layers are fairly simple if IRS techniques are used, and spectra of dilute solutions can be obtained. A correction for changes in penetration depth with frequency can be applied where needed. The signal-to-noise ratio of the spectra can be improved through additional multiple scanning and the use of a better detector. It was not feasible to study D_2O and HDO-containing solutions, but

that should be straight-forward because spectra can be recorded over the 3800 - 800 cm^{-1} range. Also, thermostatting the IRS device, so that temperature effects can be investigated, should present little difficulty. It would thus seem that IRS techniques, especially in conjunction with a Fourier transform spectrometer and digital data handling techniques, affords a useful approach to the study of structural effects with associated liquids.

ACKNOWLEDGMENT

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Quantitative Analysis of Aqueous Nitrite/Nitrate Solutions by Infrared Internal Reflectance Spectrometry

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Infrared spectra of aqueous NO_2^- and NO_3^- solutions, and of binary mixtures, were recorded using internal reflection techniques and a Fourier transform spectrometer. NO_2^- could be detected at a concentration of 0.02M, and NO_3^- at 0.001M. However, NO_3^- also became adsorbed on the Ge prism. After making corrections for NO_3^- adsorption and for overlapping of NO_2^- and NO_3^- bands, it was possible to analyze binary mixtures with concentrations as low as $[NO_3^-]$ = 0.03M and $[NO_2^-]$ = 0.05M. By adjusting the optics so that the usually totally absorbing water stretching band had a transmittance of about 50%, it was possible to observe N–H and C–H stretching bands of solutes. Dissolved materials cause the water structure and consequently the water absorption to change, causing distortions of the background of ratioed spectra of aqueous solutions. These distortions may influence qualitative and quantitative observations.

The utility of infrared internal reflection spectrometry (IRS) in providing information about adsorption from organic solvent at the liquid–solid interface (*1*) led us to attempt to study adsorption from aqueous solution, using a Ge IRS prism as adsorbent as well as for optical purposes. NO_3^- became adsorbed on Ge, prompting us to examine the quantitative aspects of the infrared analysis of aqueous solutions of NO_3^-, NO_2^-, and of NO_3^-–NO_2^- mixtures.

IRS analysis of aqueous $NaNO_3$ solutions has been described by Katlafsky and Keller (*2*), who found a linear variation, $[NO_3^-] = aA(NO_3^-)$, of the 1335-cm^{-1} NO_3^- absorbance over the 5–20% concentration range. $A(NO_3^-)$ is the NO_3^- absorbance. Wilhite and Ellis (*3*), using IRS, reported a similar linear variation for the 0.1–1M NO_3^- range, but another linear relation, $[NO_3^-] = b + cA(NO_3^-)$, for the 0.01–0.1$M$ NO_3^- range. Ahlijah and Mooney (*4*) used IRS to analyze aqueous $NaNO_3$–$NaNO_2$ solutions; their calibration plots were linear but their graphs (*5*) show them to be $[NO_3^-] = d + eA(NO_3^-)$ and $[NO_2^-] = f + gA(NO_2^-)$. Values of d and f are near 0.08 and 0.1 absorbance. As our observations differ somewhat from those made earlier, and the method is of potential utility, we describe our IRS study of aqueous NO_3^+, NO_3^-, and NO_3^-–NO_2^- solutions.

EXPERIMENTAL

A trapezoidal Ge single-pass plate, 52 × 20 × 1 mm, was used in conjunction with a suitable variable-angle attachment described elsewhere (*1*). Spectra having a constant resolution of 8 cm^{-1} were recorded with a modified Digilab Model FTS-14 Fourier transform spectrometer (*6*). All single-beam spectra were obtained by summing 400 interferograms. After the cell containing

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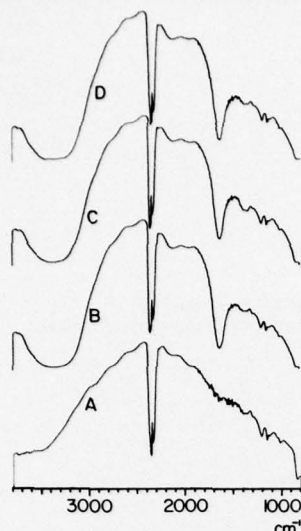
Figure 1. Single-beam spectra

(A) Dry Ge plate in empty cell; (B) water; (C) aqueous solution 0.2*M* in NaNO₃ and 0.2*M* in NaNO₂; (D) aqueous solution 0.03*M* in NaNO₂ and 0.05*M* in NaNO₃

Figure 2. Ratioed spectra

Each spectrum shown was obtained by ratioing two of the spectra of Figure 1. (A) water (B, Figure 1/A, Figure 1); (B) 0.2*M* NaNO₂ + 0.2*M* NaNO₃ solution (C, Figure 1/A, Figure 1); (C) 0.2*M* NaNO₂ + 0.2*M* NaNO₃ solution (C, Figure 1/B, Figure 1); (D) 0.03*M* NaNO₂ + 0.05*M* NaNO₃ solution (D, Figure 1/B, Figure 1)

Figure 3. Scale-expanded spectra

(A) "100% line"; see text; (B) 0.2*M* NaNO₂ + 0.2*M* NaNO₃ solution; scale-expanded segment of spectrum B of Figure 2. (C) 0.03*M* NaNO₂ + 0.05*M* NaNO₃ solution; scale-expanded segment of spectrum D of Figure 2

the Ge plate was installed, the sampling compartment was flushed with dry air. The cell remained in place throughout a series of measurements so that its transmittance remained constant; small changes in cell position can cause transmittance changes which can affect the results obtained when two single-beam spectra are ratioed. Also, the measured band intensities are dependent on factors such as the angle of incidence, beam convergence, detailed crystal geometry, and crystal index, which remained constant because a single experimental setup was used; band intensity values would change if a different setup were to be used. Pure water or solutions of various NH_4NO_2, NH_4NO_3, $NaNO_3$, $NaNO_2$, or $NaNO_2$ concentrations, prepared from distilled water and reagent-grade chemicals, were placed into the cell or were withdrawn from it by means of syringes and Teflon (DuPont) tubing was permanently attached to the cell.

RESULTS AND DISCUSSION

Only single-beam spectra were measured. These were stored by the instrument's disk memory, retrieved, and ratioed by computation as required, using the instrument's digital computer. Some examples of single-beam spectra are shown in Figure 1. The equivalent penetration depth (7), computed by taking the molar extinction coefficient of liquid water to be 81 at 3450 cm^{-1} (8), was 3.1 μ at 3450 cm^{-1} and about 8 μ at 1600 cm^{-1}. Spectrum A is the "background" of the Ge plate in air. There were prominent CO_2 bands, and some water vapor bands in the 1900–1400 cm^{-1} region, caused by residual water vapor in the spectrometer. When water was in contact with the Ge plate, the prominent OH stretching and deformation bands were superimposed on the background (B, Figure 1). The single-beam spectra of dilute solutions (C, D, Figure 1) are similar to the spectrum of water; the bands of the solute are not prominent. The instrument function was removed when two such single-beam spectra were ratioed. If the empty cell was used as reference, the ratioed spectra had the appearance of spectra obtained by the usual double-beam operation, *e.g.*, A, B, Figure 2. When water was used as the reference, the ratioed spectra had the appearance of double-beam, solvent-compensated spectra (C, D, Figure 2). The slight CO_2 bands which appeared in some spectra were brought about by changes in
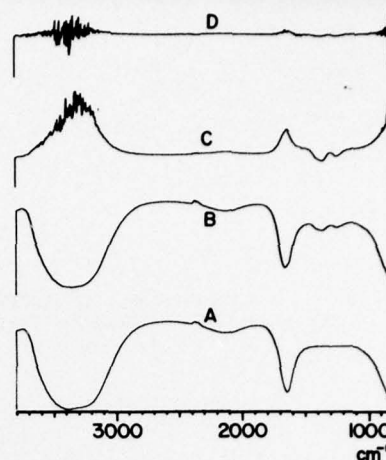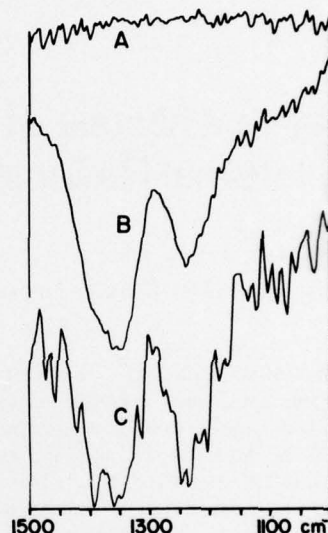
(7) N. J. Harrick, "Internal Reflection Spectroscopy." Interscience, New York, N.Y., 1967.
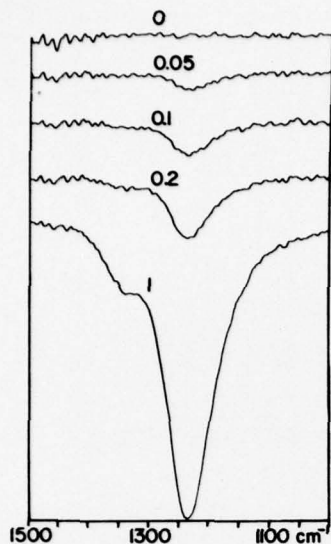(8) W. K. Thompson, *Trans. Faraday Soc.* **61**, 2635 (1965).

the efficiency of the air dryer. The noise above 3000 cm^{-1} and below 1000 cm^{-1} in spectra C and D of Figure 2 was the result of ratioing spectra in regions where the transmittance was very low. In spectrum C, the negative OH stretching band, the negative OH deformation band, and the increase in absorption below 1000 cm^{-1}, which are barely detectable in spectrum D, are not artifacts. These changes were caused by variations in the absorptivity of the water present in the solution, the water structure being affected by the solutes.

The absorptions of NO_3^- and NO_2^-, barely detectable in the single-beam spectra, became more recognizable in the ratioed spectra (A, B, Figure 2); computer-produced scale expansion then made the bands usable. Examples are shown in Figure 3. Trace A of that figure was obtained by recording two single-beam spectra of water and ratioing them against one another, in order to obtain an estimate of the noise level; it can be taken as a "100% line." Spectrum B shows the NO_3^- and NO_2^- bands. Spectrum

Figure 4. Spectra of NH_4NO_2 solutions. The numbers next to each trace indicate the molar concentrations
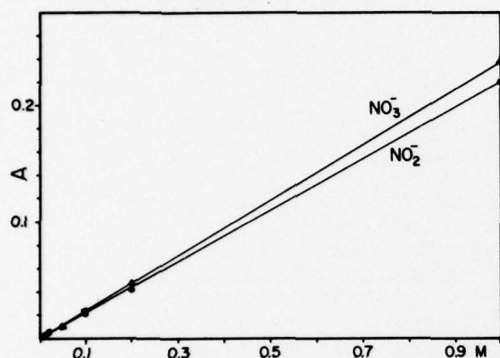

Figure 5. Calibration curves

C is a highly scale-expanded segment of spectrum D of Figure 2, plotted to the same scale as spectrum C of Figure 3; the noise level is consequently higher.

The ratioing and scale-expansion techniques outlined were used to examine single and binary solutions of various concentrations. Some segments of spectra of NH_4NO_2 solutions are shown in Figure 4. Similar results were obtained with $NaNO_2$ solutions, the intensity of the 1237-cm^{-1} NO_2^- band decreasing progressively with decreasing NO_2^- concentration. A reasonably linear relation between the absorbance of the 1237-cm^{-1} band and NO_2^- concentration was obtained (Figure 5). The lowest concentration yielding a usable spectrum was $0.02M$.

Similar measurements were carried out with NO_3^- solutions. Some results obtained with $NaNO_3$ are shown in Figure 6. The intensity of the NO_3^- band decreased progressively as the NO_3^- decreased, but remained constant at concentrations less than $0.001M$ (Figure 6A).

With relatively concentrated solutions, the NO_3^- band was broad and had a maximum at 1352 cm^{-1} and a shoulder near 1400 cm^{-1} (Figure 6B). (The weak symmetric stretching band of NO_3^- could also be observed near 1050 cm^{-1} with $1M$ NO_3^- solutions.) When the NO_3^- concentration declined, the 1400-cm^{-1} absorption diminished and the maximum of the residual, sharp band shifted to 1350 cm^{-1}. The NO_3^- band of the more concentrated solutions is more like that of solid $NaNO_3$, for which the asymmetric stretching band is at 1374 cm^{-1} (9).

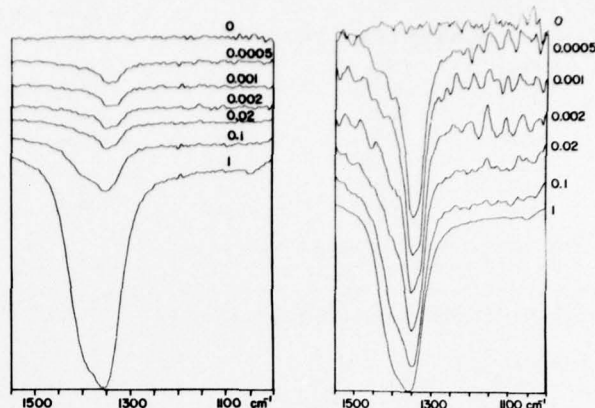(9) M. Anbar, M. Halman, and S. Pinchas, *J. Chem. Soc.*, **1960**, 1242.

Figure 6. Spectra of $NaNO_3$ solutions
The numbers next to each trace indicate $[NO_3^-]$ in M. All spectra are scale-expanded. Part A shows segments taken from a series of spectra, all spectra of the series being scale-expanded by the same factor; band intensity is consequently proportional to concentration. The same segments are shown again in Part B. In order to make changes in band contour more detectable, only the absorption in the 1550–1000 cm^{-1} range was expanded. For each segment, the lowest absorption within that range was placed at the bottom of the chart and the highest absorption at the top of the chart, so that the peak heights are the same. The expansion factor is different for each segment and is supplied by the computer

The sharp residual NO_3^- band, which could not be diminished by extensive flushing with water but which could be removed by treating the Ge plate with hot chromic acid cleaning solution, is attributed to an NO_3^- species fairly strongly bound to the Ge surface. Using the absorbance of the residual peak, and assuming that the species causing the band was NO_3^-, and that the area of the Ge plate was 20 cm^2, leads to an estimate of one adsorbed unit per 5–10 Å of surface.

The total NO_3^- absorbance at 1352 cm^{-1} could be corrected by subtracting the absorbance of the residual band of the adsorbed material. When this was done, the absorbance of NO_3^- in solution was found, and a reasonably linear relation between the corrected absorbance values and NO_3^- concentration was obtained (Figure 5). From that plot, the absorbance of the residual band (0.0111) is equivalent to the absorbance of $\sim 0.05M$ NO_3^- solution. Using the extinction coefficient of NO_3^- for the adsorbed species and estimating an equivalent penetration depth of about 7 μ at 1350 cm^{-1} leads to an estimate that the absorbance of the adsorbed species was equivalent to the absorbance of a solution of about $0.06M$ NO_3^-, in fair agreement with the value obtained from the NO_3^- calibration curve.

However, the calibration plots of Figure 5 cannot be used directly for estimating the concentrations of NO_3-NO_2^- mixtures. The 1237-cm^{-1} NO_2^- band (asymmetric stretching) has a shoulder at 1340 cm^{-1} (symmetric stretching) which, as shown clearly by Figure 7, overlapped the 1352-cm^{-1} NO_3^- band. The latter does not cause the absorbance of the 1237-cm^{-1} NO_2^- band to change significantly. The ratio of the absorbance at the 1340-cm^{-1} shoulder and that of the 1237-cm^{-1} band is about 4:21. Taking the ratio of the absorbances of the NO_2^- asymmetric and symmetric stretching bands to be constant then gives [absorbance at 1352 cm^{-1} due to NO_3^-] = [total absorbance at 1352 cm^{-1}] − [absorbance at 1237 cm^{-1}/5.25].

Some results obtained with dilute solutions are summarized in Table I. The correction for NO_3^- has been made. The agreement between actual and found values is not

Table I. Analysis of NaNO₃–NaNO₂ Solutions

M NO_2^- actual	M NO_3^- actual	M NO_3^- found	M NO_3^- found[a]
0.20	0.20	0.20	0.21
0.050	0.050	0.059	0.058
0.050	0.150	0.064	0.18
0.15	0.050	0.14	0.06
0.050	0.030	0.044	0.033

[a] Corrected for adsorption and band overlapping.

Table II. Absorptions of NaNO₂ and NaNO₃

IRS						
This work	Katlafsky and Keller (2)	Ahlijah and Mooney (4)	Transmittance (11)	Transmittance (9, 12)		Assignment
1352	1335	1333	1370	1385	NO_3^-	asym. stretch
1047		1045	1050	1049		sym. stretch
1340		1316		1335	NO_2^-	asym. stretch
1237	1225	1220		1240		sym. stretch

unreasonable. If the correction for the band overlapping had not been made, the NO_3^- concentration values would have been too high by about ⅕ of the concentration of NO_2^-. It is pertinent to note that the lowest concentrations reported earlier (4) for a binary mixture were $[NO_2^-] = 0.7M$, $[NO_3^-] = 0.5M$, 14 and 17 times as great as the lowest values in Table I.

There are considerable differences in the frequencies of the NO_3^- and NO_2^- absorptions which have been reported; a summary is given in Table II. The dispersion of the index of refraction in the infrared region is known (7); *i.e.*, in the vicinity of an absorption band, the index of refraction first decreases, then increases sharply, and decreases again to approach the normal value after the absorption has been passed. Consequently, with IRS, the penetration depth reaches a maximum when the index of refraction reaches a maximum and absorption increases. When the sine of the incident angle is very close to the ratio of the refractive indices, the absorption band maximum is distorted toward lower frequency.

In the present experiments, Ge and an average angle of incidence more than 60° were employed. The sine of the incident angle and the refractive index ratio of the Ge and liquid are far apart (0.87 and 0.33). The effect of the dispersion of the refractive index of the aqueous solution on the absorption band positions was therefore negligible. However, Katlafsky and Keller (2) used an Irtran-2 plate with an incident angle of 40°. The critical angle for the system ZnS(Irtran-2)–H₂O in the infrared range is 37.5%. Consequently, the incident angle was quite close to the critical angle, and any dispersion of the refractive index would cause a shift of absorption band maxima. Similarly, Ahlijah and Mooney (4, 10) used a KRS-5 plate and stated that the incident angle was 30°. However, the critical angle for the KRS-5–H₂O system is 33.7°, the refractive index of KRS-5 and H₂O being taken as 2.4 (7) and 1.33, respectively. Their measurements must have been made with the incident angle close to the critical angle, so that, again, band distortions occurred. The low values of band positions reported by Katlafsky and Keller and by Ahlijah and Mooney can be attributed to such band distortions.

(10) G. E. B. Y. Ahlijah, and E. F. Mooney, *Spectrochim. Acta.* **22A**, 547 (1966).
(11) L. V. Volod'ko and L. T. Huoah, *Zh. Prikl. Spektrosk.*. **9**, 644 (1968).
(12) R. E. Weston, Jr., and T. F. Brodasky, *J. Chem. Phys.*. **27**, 683 (1957).
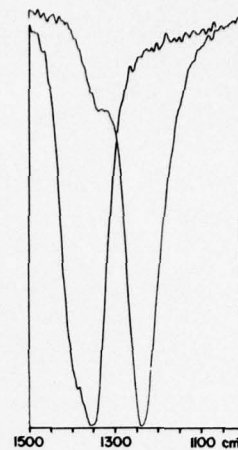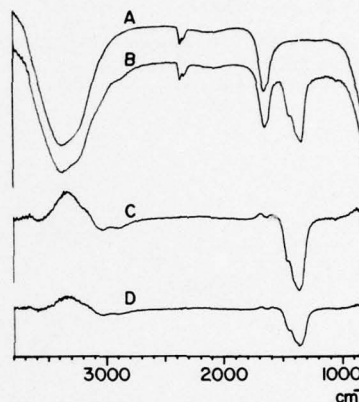
Figure 7. Spectra of NO_3^- and NO_2^-

Figure 8. Spectra of H_2O and NH_4NO_3 solutions

(A) Water; (B) 2M NH_4NO_3 solution. The reference used for the ratioed spectra A and B was the single-beam spectrum of the dry Ge. (C) 2M NH_4NO_3 solution, the ratio of spectra B and A. (D) 1M NH_4NO_3 solution, the ratio of a spectrum (of 1M NH_4NO_3 solution similar to spectrum C) and spectrum A
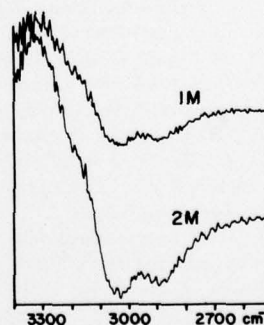

Figure 9. Spectra of NH_4^+. Scale-expanded segments of spectra C and D of Figure 8

It was of interest to determine how well spectral features of dissolved materials could be discerned in the vicinity of the intense water stretching band. Consequently, the incident angle was adjusted to decrease the penetration depth to about 0.8 μ at 3400 cm⁻¹. The spectra of Figure 8 were then recorded.

The water stretching band (A, Figure 8), obtained at about 50% maximum transmittance, has the same contour as the band observed by transmittance measurements by

Thompson *et al.* (*13*). Two broad absorptions due to NH_4^+ (8) appear on the low-wavenumber side of the OH band in the $3100–2600$ cm^{-1} region when NH_4NO_3 is dissolved in the water (B, Figure 8), and these become more prominent when the spectra are solvent-compensated (C, D, Figure 8) and then scale-expanded (Figure 9). There is, however, some distortion of the 3050-cm^{-1} band because of the negative OH band. The distortion decreases as the solute concentration is decreased, but this also decreases the solute band. Consequently, as the liquid layer is necessarily thin as well as dilute, the signal-to-noise ratio decreases. With the present technique, the lowest concentrations at which N–H and C–H bands (similar experiments were made with aqueous methanol, Na citrate, etc.) were observed were near $0.1M$.

(13) W. K. Thompson, W. A. Senior, and B. A. Pethica, *Nature (London)*, **211**, 1086 (1966).

The results thus show that it is feasible to obtain spectral information near or even at the position of one of the strong water absorptions. It must be kept in mind, however, that the presence of solutes causes the water bands to change in absorption, so that distortions result. Such distortions may also affect quantitative results by causing base lines to fluctuate. The distortions decrease in intensity with decreasing solute concentration. However, because their intensities and frequencies are a function of the nature of the solute, they cannot be precisely compensated.

Infrared internal reflection spectra of methanol–water mixtures

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Abstract—Infrared spectra of 0–100 vol% methanol–water mixtures were recorded over the 3900–900 cm^{-1} range at 8 cm^{-1} resolution using internal reflection techniques and a Fourier transform spectrometer. There were interactions of the water and methanol which made themselves evident as changes of the water OH stretching and deformation band frequencies. The methanol band frequencies were unaffected by changes in concentration and consequently those bands can be used for quantitative purposes, but water bands should not be used for precise determinations.

INTRODUCTION

MALONE and FLOURNOY have measured infrared internal reflection spectra of aqueous solutions of methanol, ethanol, *n*-propanol, and *i*-propanol, and reported that Beer's Law concentration dependencies were obtained over 0–100% concentration ranges, so that the measurements would be useful as a quantitative analytical procedure [1]. No band frequency changes were observed, except for the skeletal bands of *n*-propanol, and they commented that " . . . no explanation has been derived for the surprisingly linear relationships found for these non-ideal solutions" [1]. As they pointed out for the case of methanol–water mixtures, the absence of detectable shifts in vibrational frequencies over the wide range of concentrations indicates that there were no significant changes in intermolecular bonding. However, these general observations conflict with earlier ones made with ethanol–water mixtures: SZEPESY *et al.*, recorded transmission spectra of ethanol–water mixtures in the overtone region and reported finding Beer's Law deviations which they attributed to ethanol–water interactions [2]. Also, SPINK and WYCKOFF measured near-infrared differential spectra of several simple alcohols in aqueous solution and found changes in the 860–1020 nm region which they used to derive the apparent hydration numbers of the alcohols [3].

This discrepancy was of interest to us because changes in solute–solvent interactions are pertinent to our infrared studies of adsorption phenomena occurring at the liquid–solid interface [4]. As we contemplated using adsorbates dissolved in methanol–water mixtures, the methanol–water system was reinvestigated.

EXPERIMENTAL

Internal reflection techniques were employed using a Ge prism in a suitable attachment [4]. The incident angle was adjusted to give an equivalent penetration

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[1] C. P. MALONE and P. A. FLOURNOY, *Spectrochim. Acta* **21**, 1361 (1965).
[2] G. L. SZEPESY, J. CSASZAR, and L. LEHOTAI, *Acta Univ. Szegediensis, Acta Phys. et Chim.* **2**, 149 (1956).
[3] C. H. SPINK and J. C. WYCKOFF, *J. Phys. Chem.* **76**, 1660 (1972).
[4] R. T. YANG, M. J. D. LOW, G. L. HALLER, and J. FENN, *J. Colloid, Interface Sci.* **44**, 249 (1973).

depth of $0.85\ \mu$m at 3300 cm^{-1}. Spectra having a constant resolution of 8 cm^{-1} were recorded with a modified Digilab, Inc. Model FTS–14 Fourier transform spectrometer [5]. All single-beam spectra were obtained by summing 400 interferograms.

After the cell containing the prism was installed, the sampling compartment was flushed with dry air. The cell remained in place throughout the series of measurements so that its transmission remained constant; small changes in cell position can cause transmission changes which can affect the results obtained when two single-beam spectra are ratioed. Aqueous solutions of 0, 10, 25, 50, 75 and 100 vol% methanol, prepared with spectral-grade absolute methanol and distilled water, were placed into the cell or withdrawn from it by means of syringes and Teflon tubing. Solutions of reagent-grade NaClO$_4$ in methanol were similarly treated.

RESULTS AND DISCUSSION

Single-beam spectra were stored, recalled, and ratioed by computation as required, using the instrument's digital computer. Some examples are shown in Fig. 1. The ratioing process is equivalent to using a dispersion spectrometer in the
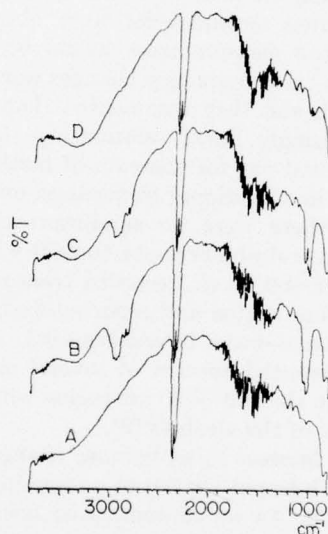

Fig. 1. Single-beam spectra: A: dry cell. B: pure methanol. C: 50% methanol in water. D: pure water.

double-beam mode with cells of precisely the same optical quality and path lengths in each beam, thus "compensating" one liquid with another. This equivalency is correct only when the two liquids whose spectra are ratioed have identical refractive indices, so that the equivalent penetration depths for the two liquids are the same. In the present case, with the indices of refraction at 25° of water and methanol of 1.332 and 1.326, respectively, the penetration depths differ by less than 0.1%. Also, the index matching is good, the high refractive index of the Ge prism causing any

[5] M. J. D. LOW, A. J. GOODSEL, and H. MARK, in *Molecular Spectroscopy* (1971), (edited by HEPPLE P.) *Proc.* 5th *Conf. Molecular Spectroscopy*, Brighton, England, 1971. Institute of Petroleum, London, 1972; pp. 383ff.

effects due to variation of the refractive index of the sample to be very small. At low absorptivity the variation of the refractive index in the absorption band is also negligible. Consequently, possible errors caused by these effects can be neglected.

The single-beam spectra of the pure liquids or solutions can be ratioed against "air," i.e., against the spectrum of the empty cell, to obtain spectra such as A, B, or C of Fig. 2, in which the instrument function has been removed. The contour of the
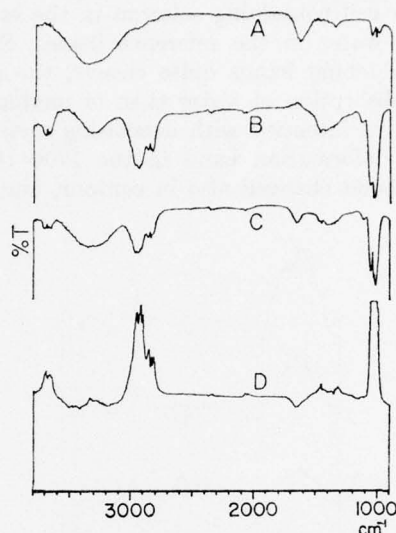

Fig. 2. Ratioed spectra: A: water ratioed against air (the ratio of spectra D and A of Fig. 1). B: methanol ratioed against air (the ratio of spectra B and A of Fig. 1). C: 50% methanol solution ratioed against air (the ratio of spectra C and A of Fig. 1). D: 75% methanol solution ratioed against methanol (the ratio of the single-beam spectrum of a 75% methanol solution similar to spectrum C of Fig. 1 against spectrum B of Fig. 1).

OH stretching band (A, Fig. 2) is like that of the infrared transmission spectrum of a thin water layer reported by THOMPSON et al, [6], who concluded that there were three strongly overlapping bands at 3625, 3410 and 3250 cm^{-1}. The OH band (A, Fig. 2) is also similar to the Raman OH band [7], but differs from that of BONNER and CURRY [8, 9]. The spectra of water, methanol, and water–methanol solution

[6] W. K. THOMPSON, W. A. SENIOR, and B. A. PETHICA, *Nature, Lond.* **211**, 1086 (1966).

[7] W. F. MURPHY and H. J. BERNSTEIN, *J. Phys. Chem.* **76**, 1147 (1972).

[8] O. D. BONNER and J. D. CURRY, *Infrared Physics* **10**, 91 (1970).

[9] BONNER and CURRY [8] recorded differential spectra of water using two cells of nominally 0·007 mm pathlength but differing in actual pathlength by 5–10%, and found two quite definite bands at 3530 and 3200 cm^{-1} (2625 and 2418 cm^{-1} with D_2O). Their "effective thickness" of liquid yielding their differential spectra was of the order of 0·0005 mm, i.e., close to the effective penetration depth of 0·00085 mm in the present work. However, the actual thickness of their liquid was near 0·007 mm, and a single layer of it had a transmittance close to zero near 3400 cm^{-1}. The cause of the differences in the OH bands is not known. Possibly, the change in the refractive index in the region of intense absorption caused changes in the absorptive, refractive, and reflective properties of the thin films; or possibly, the relatively fast scan rates used in regions of high absorption caused some distortion.

(A, B, C, Fig. 2) are thus similar to those of MALONE and FLOURNOY (Fig. 2 of reference 1), who had an attachment with a Ge–liquid interface in the sample beam and an identical attachment with a Ge–air interface in the reference beam [1].

When the single-beam spectra are ratioed against those of the pure solvents, solvent-compensated spectra such as those of Fig. 3 are obtained. Such spectra are similar to the differential absorption spectra of Spink and Wyckoff (Fig. 1 of reference 3), who used a cell containing solution in the sample beam and had a matched cell containing water in the reference beam. Spectrum A shows the difference in the OH stretching bands quite clearly, the negative band being a measure of the greater absorption of water than of methanol. The negative OH stretching band declined in intensity with decreasing methanol concentration, as did the negative water deformation band in the 1700–1600 cm^{-1} region (A–E, Fig. 3). The stretching band changed also in contour, and the deformation band
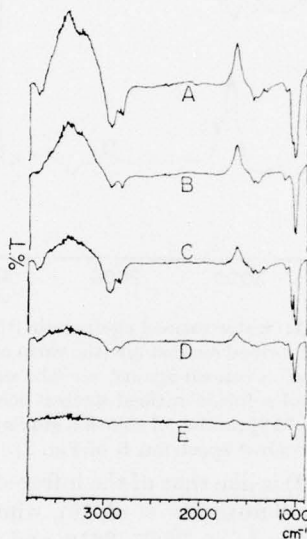

Fig. 3. Ratioed spectra using water as reference: A: pure methanol. B: 75% methanol. C: 50% methanol. D: 25% methanol. E: 10% methanol. In each case, the reference spectrum was that of pure water; e.g., spectrum A is the result of the ratio of spectra B and D of Fig. 1.

shifted in frequency, being at 1640 cm^{-1} for pure water, 10% and 25% methanol solutions, near 1650 cm^{-1} for 50% methanol solution, and near 1660 cm^{-1} for 75% methanol solution. Such changes can be clearly seen in scale-expanded segments of spectra such as Fig. 4. However, the 1460 cm^{-1} OH deformation band of methanol did not shift, and there were no changes in the positions of the other methanol bands, when the methanol concentration was varied.

The changes in the negative OH stretching band merely indicate the net changes in absorption; both the absorption caused by water and the absorption caused by
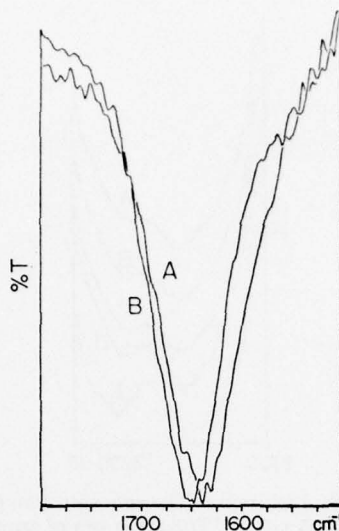
Fig. 4. Water deformation bands: Scale-expanded segments of spectra of water (A) and of 50% methanol solution (B). The spectrum of methanol was used as reference. The ordinates were expanded so that the two bands had the same intensities.

the methanol hydroxyls might change. However, the change in frequency of the water deformation band (which implies that some change occurred in the inter-molecular bonding of the water), and the constancy of the frequency of the methanol hydroxyl deformation band (which implies that the strength of the intermolecular bonding was not affected), suggest that the changes of the contour of the negative OH stretching band were brought about mainly by changes of the absorption of the water component of the solutions. If the contour of the methanol band is unaffected, it would be more appropriate to compare the spectra of solutions with the spectrum of pure methanol, as in trace D of Fig. 2, which shows the OH stretching absorption as a pair of positive bands. In contrast, Malone and Flournoy obtained the intensities of the water OH and methanol OH absorptions (both were taken to occur at 3350 cm^{-1}) by a simple subtraction procedure; for each wavelength, the absorbance due to water was subtracted from the total to give that due to methanol alone.

Scale-expanded segments showing the OH stretching regions of spectra such as D of Fig. 2 are collected in Fig. 5. The segments were scale-expanded to identical maximum and minimum ordinate values in order to bring out the changes in band contours more clearly. There were slight differences among the spectra of the 0, 10 and 25% solutions, and somewhat larger changes with the 50 and 75% solutions.

The present results thus show that interactions between water and methanol did not affect the methanol bands, so that these can be used for quantitative purposes, but that the water stretching and deformation bands were changed, so that these should not be used. It seems probable that similar effects would occur with other alcohol–water mixtures.
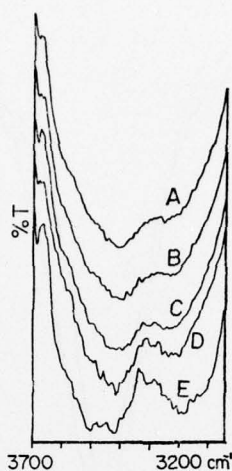
Fig. 5. Spectra of methanol solutions: The concentration of methanol was: A, O; B, 10; C, 25; D, 50; E, 75 vol.%. The spectrum of pure methanol was used as reference.

Glew has been able to measure the infrared spectra of dilute water in various solvents. With concentrated water, however, the intense absorption of water and the overlapping of the bands of water and solvent made the observations and interpretations difficult [10]. It seems worth noting that the present techniques enable water to be examined at any concentration.

[10] D. N. Glew, in *Hydrogen–Bonded Solvent Systems*, p. 133. (edited by Covington A. K. and Jones, P.), Taylor & Francis, London, 1968.